

AD-A257 309



AD-A257 309
Copy 9 of 35 copies

(2)

IDA DOCUMENT D-1174

THE DARPA HIGH-PERFORMANCE POLYMER PROGRAM

Volume II. Appendix--Selected Presentation Material From the
Program Review Held on 14-15 January 1992

David R. Squire, *IDA Consultant*
Loker Hydrocarbon Research Institute
University of Southern California

George Mayer
Institute for Defense Analyses

DTIC
ELECTE
NOV 13 1992
S A D

September 1992

Prepared for
Defense Advanced Research Projects Agency

92-29699



Approved for public release; distribution unlimited.



INSTITUTE FOR DEFENSE ANALYSES
1801 N. Beauregard Street, Alexandria, Virginia 22311-1772

DEFINITIONS

IDA publishes the following documents to report the results of its work.

Reports

Reports are the most authoritative and most carefully considered products IDA publishes. They normally embody results of major projects which (a) have a direct bearing on decisions affecting major programs, (b) address issues of significant concern to the Executive Branch, the Congress and/or the public, or (c) address issues that have significant economic implications. IDA Reports are reviewed by outside panels of experts to ensure their high quality and relevance to the problems studied, and they are released by the President of IDA.

Group Reports

Group Reports record the findings and results of IDA established working groups and panels composed of senior individuals addressing major issues which otherwise would be the subject of an IDA Report. IDA Group Reports are reviewed by the senior individuals responsible for the project and others as selected by IDA to ensure their high quality and relevance to the problems studied, and are released by the President of IDA.

Papers

Papers, also authoritative and carefully considered products of IDA, address studies that are narrower in scope than those covered in Reports. IDA Papers are reviewed to ensure that they meet the high standards expected of refereed papers in professional journals or formal Agency reports.

Documents

IDA Documents are used for the convenience of the sponsors or the analysts (a) to record substantive work done in quick reaction studies, (b) to record the proceedings of conferences and meetings, (c) to make available preliminary and tentative results of analyses, (d) to record data developed in the course of an investigation, or (e) to forward information that is essentially unanalyzed and unevaluated. The review of IDA Documents is suited to their content and intended use.

The work reported in this document was conducted under contract MDA 903 89 C 0003 for the Department of Defense. The publication of this IDA document does not indicate endorsement by the Department of Defense, nor should the contents be construed as reflecting the official position of that Agency.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public Reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188) Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE September 1992	3. REPORT TYPE AND DATES COVERED Final--December 1991 to July 1992
4. TITLE AND SUBTITLE The DARPA High-Performance Polymer Program, Volume II: Appendix--Selected Presentation Material from the Program Review Held on 14-15 January 1992			5. FUNDING NUMBERS C - MDA 903 89 C 0003 T- A-131
6. AUTHOR(S) David R. Squire, George Mayer			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Institute for Defense Analyses 1801 N. Beauregard St. Alexandria, VA 22311-1772			8. PERFORMING ORGANIZATION REPORT NUMBER IDA Document D-1174, Vol. II
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Defense Advanced Research Projects Agency 3701 North Fairfax Drive Arlington, VA 22203-1714			10. SPONSORING/MONITORING AGENCY REPORT NUMBER
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12b. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 words) In a series of projects dating back to 1984, the Defense Advanced Research Projects Agency (DARPA) has instigated research in advanced polymers including such goals as thermally oxidatively stable matrix resins for 700°F composite applications, rigid molecular composites, liquid crystal displays, and piezoelectric sensors. Volume I of the present report reviews the history and accomplishments of the DARPA High-Performance Polymer Program and presents highlights of the program review conducted by DARPA on 14-15 January 1992. Volume II, intended as a comprehensive reference source document, is an appendix which provides the program review agenda, a list of participants, and copies of selected presentation material. Correspondence from the presenters is included with the presentation material where appropriate.			
14. SUBJECT TERMS polymers, composite materials, matrix materials			15. NUMBER OF PAGES 675
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT SAR

IDA DOCUMENT D-1174

THE DARPA HIGH-PERFORMANCE POLYMER PROGRAM

Volume II. Appendix--Selected Presentation Material From the
Program Review Held on 14-15 January 1992

David R. Squire, *IDA Consultant*
Loker Hydrocarbon Research Institute
University of Southern California

George Mayer
Institute for Defense Analyses

September 1992

DTIC QUALITY INSPECTED 4

Approved for public release; distribution unlimited.



INSTITUTE FOR DEFENSE ANALYSES

Contract MDA 903 89 C 0003
DARPA Assignment A-131

Accession For	
NTIS	CRA&I <input checked="" type="checkbox"/>
DTIC	TAB <input type="checkbox"/>
Unannounced <input type="checkbox"/>	
Justification	
By	
Distribution/	
Availability Code	
Dist	Avail
A-1	

FOREWORD

This document was prepared for the Materials Science Division, Defense Sciences Office, Defense Advanced Research Projects Agency, as part of Project Assignment A-131 under the technical cognizance of Dr. Richard T. Loda.

While this document has not been subjected to a formal IDA review, it has been read by IDA and DARPA personnel and is believed to be an accurate account.

PREFACE

Volume I of this IDA Document provides the background of the DARPA High-Performance Polymer Program along with highlights of the program review held by DARPA on 14-15 January 1992. The present Volume II appends the program review agenda, a list of participants, and copies of the presentation material. Volume II is meant only as a reference source and contains no further discussion than the unedited material from the presentations.

The presentation material, including correspondence from the presenters where appropriate, appears in the order of the agenda, separated by breaker pages. The material from the two University of Illinois presentations is not available.

ACKNOWLEDGMENT

The authors hereby acknowledge the yeoman service of John E. Hove, of IDA, in reviewing and substantially editing this report.

ABSTRACT

In a series of projects dating back to 1984, the Defense Advanced Research Projects Agency (DARPA) has instigated research in advanced polymers including such goals as thermally oxidatively stable matrix resins for 700°F composite applications, rigid molecular composites, liquid crystal displays, and piezoelectric sensors. Volume I of the present report reviews the history and accomplishments of the DARPA High-Performance Polymer Program and presents highlights of the program review conducted by DARPA on 14-15 January 1992. Volume II, intended as a comprehensive reference source document, is an appendix which provides the program review agenda, a list of participants, and copies of selected presentation material. Correspondence from the presenters is included with the presentation material where appropriate.

CONTENTS – VOLUME II

Foreword	iii
Preface	v
Acknowledgment	vii
Abstract	ix
I. AGENDA AND PARTICIPANTS	I-1
II. PRESENTATION MATERIAL.....	II-1
University of Massachusetts, Professor Frank E. Karasz	II-A-1
University of Pennsylvania, Professor Alan G. McDiarmid	II-B-1
Massachusetts Institute of Technology, Professor Ali S. Argon.....	II-C-1
University of Texas at Arlington, Professor Martin Pomerantz	II-D-1
University of Illinois, Dr. James Economy.....	II-E-1
Rutgers University, Professor Jerry I. Scheinbeim	II-F-1
University of Southern California, Professor William P. Weber	II-G-1
University of Southern Mississippi, Professor Charles L. McCormick	II-H-1
Hoechst Celanese Research Division, Dr. Morton M. Glick	II-I-1
University of Southern California, Professor Eric J. Amis.....	II-J-1
Virginia Polytechnic Institute and State University, Professor James E. McGrath	II-K-1
Clemson University, Professor Mark C. Thies	II-L-1
Research Triangle Institute, Dr. Jack Preston	II-M-1

I. AGENDA AND PARTICIPANTS

DARPA POLYMER PROGRAM REVIEW--JANUARY 14-15, 1992

TUESDAY, JANUARY 14

8:30-8:35	Welcoming Remarks	Ben A. Wilcox, Deputy Director Defense Sciences Office, DARPA
8:35-8:45	Introductory Remarks	Richard T. Loda, Program Manager
8:45-10:00	Univ. of Massachusetts (Karasz)	Chair, Charles Lee, AFOSR
10:00-10:15	BREAK	
10:15-12:15	Univ. of Pennsylvania (MacDiarmid)	"
12:15-1:00	LUNCH	
1:00-2:15	M.I.T. (Argon)	Chair, JoAnn Milliken, NRL
2:15-3:30	Univ. of Texas, Arlington (Pomerantz)	"
3:30-3:40	ADJOURNMENT	
3:45-5:00	Closed Advisory Session	Chair, Richard T. Loda

WEDNESDAY, JANUARY 15

8:30-9:30	Univ. of Illinois (Economy) (2)	Chair, Kenneth Wynne, ONR
9:30-10:15	Rutgers University (Scheinbeim)	"
10:15-10:30	BREAK	
10:30-11:15	Univ. of Southern California (Weber)	"
11:15-12:00	Univ. of Southern Mississippi (McCormick)	"
12:00-12:20	Hoechst Celanese (Glick)	"
12:20-1:00	LUNCH	
1:00-1:45	Univ. of Southern California (Amis)	Chair, Andrew Crowson, ARO
1:45-2:30	VPI and State University (McGrath)	"
2:30-2:45	BREAK	
2:45-3:30	Clemson University (Thies)	"
3:30-4:15	Research Triangle Institute (Preston)	"
4:15-4:20	ADJOURNMENT	
4:20-5:00	Closed Advisory Session	Chair, Richard T. Loda

**DARPA Polymer Program Review
January 14-15, 1992**

Professor Eric J. Amis
University of Southern California
Dept. of Chemistry, SSC 705
Los Angeles, CA 90089-0482
213-740-4113

Dr. Patrick Aubourg
Owens-Corning
2790 Columbus Road
Granville, OH 43023
614-587-7604

Dr. Edward Balizer
Navy Laboratory White Oak (NSWC)
Silver Spring, MD 20903-5000
301-394-1444

Dr. Kent G. Blizard
Foster-Miller, Inc.
350 Second Avenue
Waltham, MA 02154-1196
617-290-0992

Dr. Robert Boschan
Lockheed Aeronautical Systems Co.
Dept. 73C4, Zone 0150, Bldg. B1M
86 South Cobb Drive
Marietta, GA 30063
404-494-9714

Dr. Robert F. Brady
Naval Research Laboratory
4555 Overlook Avenue, SW
Code 6123
Washington, DC 20375-5000
202-767-2668

Dr. Leonard J. Buckley
Naval Air Development Center
Code 6064
Warminster, PA 18974
215-441-2823

Dr. Edward Chen
Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709
919-549-4325

Dr. Edward C. Chenevy
Hoechst Celanese
86 Morris Avenue
Summit, NJ 07901
908-522-7806

Professor Robert E. Cohen
Massachusetts Institute of Technology
77 Massachusetts Avenue
Cambridge, MA 02139-4307
617-253-3777

Dr. Andrew Crowson
Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709
919-549-4261

Dr. Ronald DeMarco
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000
703-696-5075

Dr. Mark A. Druy
Foster-Miller, Inc.
350 Second Avenue
Waltham, MA 02154-1196
617-290-0992

Dr. James Economy
University of Illinois
1304 W. Green Street
Urbana, IL 61801
217-333-1440

Professor Ronald L. Elsenbaumer
University of Texas at Arlington
Dept. of Chemistry, Box 19065
Arlington, TX 76019
817-273-3809

Professor Arthur J. Epstein
Ohio State University
Dept. of Physics
174 West 18th Avenue, Room 4108
Columbus, OH 43210-1106
614-292-1133

Professor William A. Feld
Wright State University
Chemistry Dept.
Dayton, OH 45435
513-873-2511

Dr. Morton M. Glick
Hoechst Celanese
86 Morris Avenue
Summit, NJ 07901
908-522-7768

Professor Roger D. Hester
University of Southern Mississippi
Box 10076, Southern Station
Hattiesburg, MS 89406
601-266-4868

Dr. G. Ronald Husk
Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709
919-549-4203

Dr. Brian Jensen
NASA Langley Research Center
MS 226, NASA-LaRC
Hampton, VA 23665
804-864-4271

Professor Frank E. Karasz
University of Massachusetts
Polymer Science Dept., 701 GRT
Amherst, MA 01003
413-545-4783

Dr. Teddy M. Keller
Naval Research Laboratory
4555 Overlook Avenue, SW
Code 6120
Washington, DC 20375-5000
202-767-3095

Dr. Oh-Kil Kim
Naval Research Laboratory
4555 Overlook Avenue, SW
Code 6120
Washington, DC 20375-5000
202-767-2088

Dr. Charles Lee
AFOSR/NC
Bolling AFB, DC 20332
202-767-4963

Dr. Raymond Leibfried
Hercules Research Center
Wilmington, DE 19894
302-995-3126

Dr. George A. Lo
Lockheed Missiles and Space Co.
3251 Hanover Street, Polymer Chemistry
Palo Alto, CA 94304-1191
415-424-2504

Dr. Richard T. Loda
Defense Advanced Research Projects Agency
3701 North Fairfax Drive - DSO
Arlington, VA 22203-1714
703-696-2283

Professor Alan G. McDiarmid
University of Pennsylvania
Dept. of Chemistry
343 Chemistry Building
Philadelphia, PA 19104-6323
215-898-8307

Professor William J. MacKnight
University of Massachusetts
Polymer Science Dept., 701 GRT
Amherst, MA 01003
413-545-0433

Dr. George Mayer*
Institute for Defense Analyses
1801 N. Beauregard Street
Alexandria, VA 22311-1772
703-578-2864

Professor Charles L. McCormick
University of Southern Mississippi
Box 10076, Southern Station
Hattiesburg, MS 89406
601-266-4872

Professor James E. McGrath
Virginia Polytechnic Institute & State Univ.
2111 Hahn Hall, Mail Stop 0212
Blacksburg, VA 24061-0212
703-231-5976

Dr. JoAnn Milliken
Naval Research Laboratory
4555 Overlook Avenue, SW
Code 6120
Washington, DC 20375-5000
202-767-3088

Professor Brian A. Newman
Rutgers University
Dept. of Materials Science & Engineering
P.O. Box 909
Piscataway, NJ 08855-0909
908-932-4337

Mr. Joe Piche
Foster-Miller, Inc.
350 Second Avenue
Waltham, MA 02154-1196
617-290-0992

Professor Martin Pomerantz
University of Texas at Arlington
Dept. of Chemistry, Box 19065
Arlington, TX 76019
817-273-3811

* Now at University of Pittsburgh.

Dr. Jack Preston
Research Triangle Institute
P.O. Box 12194
Research Triangle Park, NC 27709-2194
919-541-6384

Professor John R. Reynolds
University of Florida
Dept. of Chemistry
Gainesville, FL 32611
904-392-9151

Dr. Terry L. St. Clair
NASA Langley Research Center
MS 226, NASA-LaRC
Hampton, VA 23665
804-864-4273

Professor Jerry I. Scheinbeim
Rutgers University
Dept. of Materials Science & Engineering
P.O. Box 909
Piscataway, NJ 08855-0909
908-932-3669

Dr. Michael Sennett
Army Materials Technology Laboratory
Arsenal Street, SLCMT-EMP
Watertown, MA 02172-0001
617-923-5122

Dr. Desmond Sheehan
Naval Research Laboratory
4555 Overlook Avenue, SW
Code 6120
Washington, DC 20375-5000
202-767-2336

Dr. Arthur W. Snow
Naval Research Laboratory
4555 Overlook Avenue, SW
Code 6120
Washington, DC 20375-5000
202-767-5341

Dr. David R. Squire
University of Southern California
Loker Hydrocarbon Research Institute
University Park
Los Angeles, CA 90089-1661
213-740-6678

Professor Vivian T. Stannett
Research Triangle Institute
P.O. Box 12194
Research Triangle Park, NC 27709-2194
919-541-6384

Professor Mark C. Thies
Clemson University
Dept. of Chemical Engineering
Clemson, SC 29634
803-656-3056

Professor Edwin L. Thomas
Massachusetts Institute of Technology
77 Massachusetts Avenue
Cambridge, MA 02139
617-253-6901

Professor William P. Weber
University of Southern California
Loker Hydrocarbon Research Institute
University Park
Los Angeles, CA 90089-1661
213-740-5961

Dr. John West
Kent State University
Liquid Crystal Institute
Dept. of Chemistry
Kent, OH 44242-0001
216-672-2581

Dr. Ben A. Wilcox
Defense Advanced Research Projects Agency
3701 North Fairfax Drive - DSO
Arlington, VA 22203-1714
703-696-2241

Dr. Wen-li Wu
National Institute of Standards and Technology
Building 224, A209
Gaithersburg, MD 20899
301-975-6839

Dr. Kenneth Wynne
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000
603-696-4409

Mr. Joseph Zegarski
Lockheed Missiles and Space Co.
3251 Hanover Street, Polymer Chemistry
Palo Alto, CA 94304-1191
415-424-2192

II. PRESENTATION MATERIAL

UNIVERSITY OF MASSACHUSETTS

Professor Frank E. Karasz

URI REVIEW 14 JANUARY 1992

UMASS PROGRAM

- 8:45 F.E. KARASZ: OVERVIEW**
- 8:55 W. FELD (WSU): NLO AND OTHER
POLYMER SYNTHESSES**
- 9:10 F.E. KARASZ: NEW
CHARACTERIZATION TECHNIQUES;
SIMULATIONS**
- 9:30 E. THOMAS (MIT): BLOCK
COPOLYMERS**
- 9:45 M. DRUY (FMI): PROCESSING**
- 9:59 F.E. KARASZ: WRAP UP**

URI ORGANIZATION: 1991

UMASS

PSE

F.E. Karasz (P.I.)
W.J. MacKnight

CHEMISTRY

P. Lahti

PHYSICS

K. Langley

II-A-4

SUBCONTRACTORS

WRIGHT STATE UNIV

W. Feld
J. Kane

MIT

E. Thomas

FOSTER MILLER

R. Lusignea
M. Druy

OTHER URI INTERACTIONS: CELANESE, LOCKHEED,

NASA, VPI

MULTICOMPONENTS/MULTIPHASE STRUCTURAL POLYMERS

**FACULTY ASSOCIATES: Profs. MacKnight, Thomas
(MIT)**

- **CHARACTERIZATION**
- **BLENDS: PBI/PI AND PI/PES**
- **PHASE SEPARATED STRUCTURES**
- **THEORY: SIMULATIONS**

NEW POLYMERS AND CHARACTERIZATION

FACULTY ASSOCIATES: Profs. MacKnight, Langley;

Thomas (MIT)

- **IONOMERS**
- **STAR BLOCK COPOLYMER MORPHOLOGY**
(ALSO COUPLE TO BLEND SECTION)
- **DIFFUSION IN PORES: QELS AND FRS**
- **SOLID STATE NMR**

ELECTRICAL PROPERTIES OF POLYMERS

FACULTY ASSOCIATES: Prof. Lahti; Druy (FMI)

- **PPV AND DERIVATIVES; COPOLYMERS AND BLENDS**
- **PROCESSING (COUPLE TO NLO)**

NON LINEAR OPTICAL PROPERTIES

**FACULTY ASSOCIATES: Profs. Feld, Kane (WSU);
Druy (FMI)**

- **SYNTHESIS (PPV and related; LCPs)**
- **CHARACTERIZATION**
- **NLO MEASUREMENTS (with Prof. Prasad, SUNY
Buffalo)**

Department of Chemistry

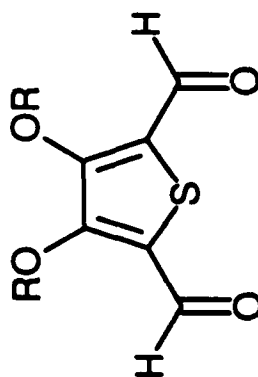
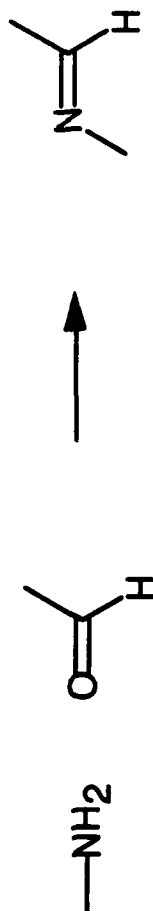
Wright State University

The Synthesis of Unique NLO Active Small Molecules, Monomers, and Polymers

***William A. Feld
Department of Chemistry
Wright State University
Dayton, OH 45435***

- *Thiophene-Azomethines*
- *Thiophene-Enynes*
- *3,4-Dialkoxythiophenes*
- *Tetrazines*

Thiophene Azomethines

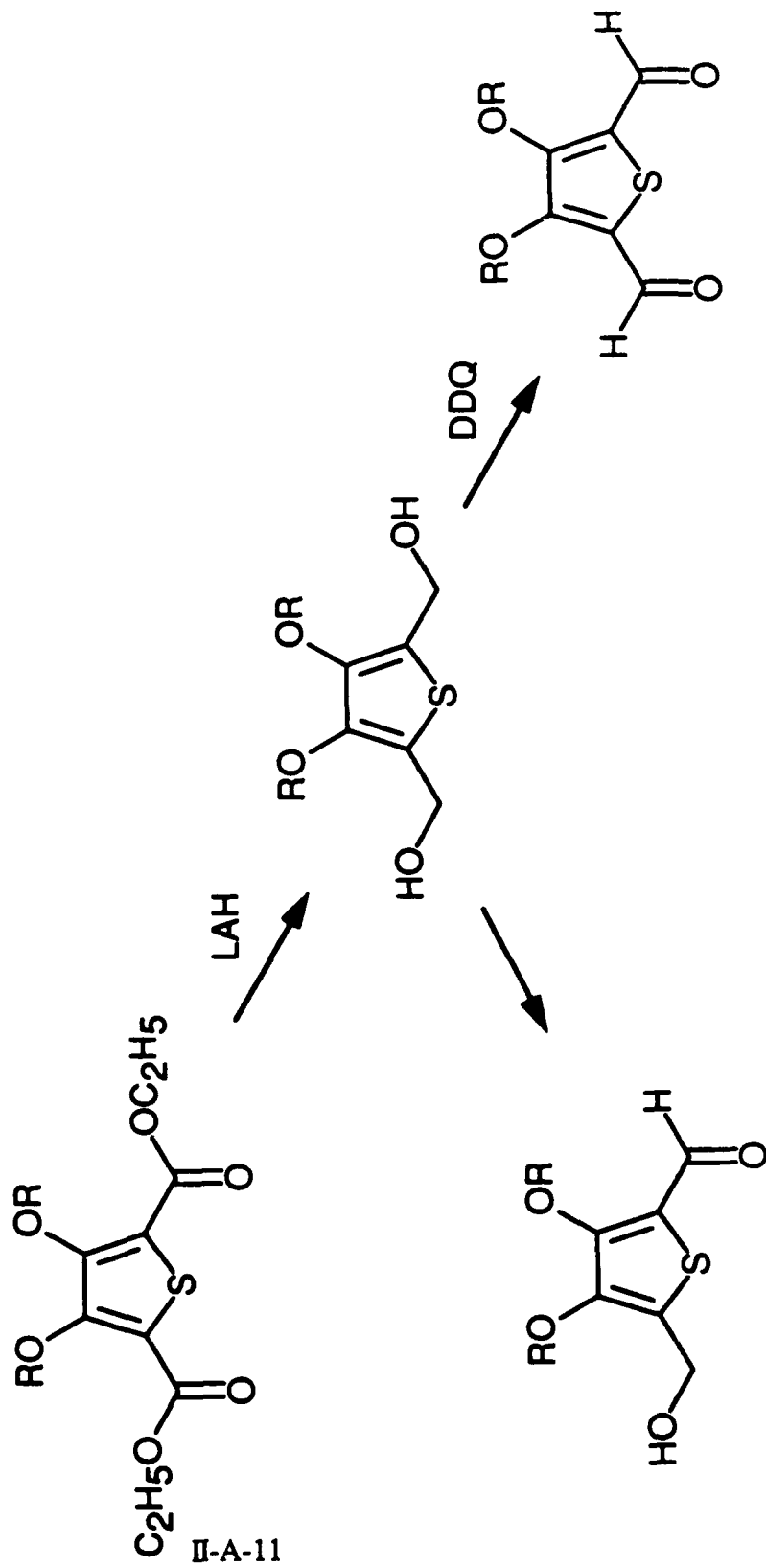


New Synthesis

Polymer Preprints, 1992, **33**, xxxx

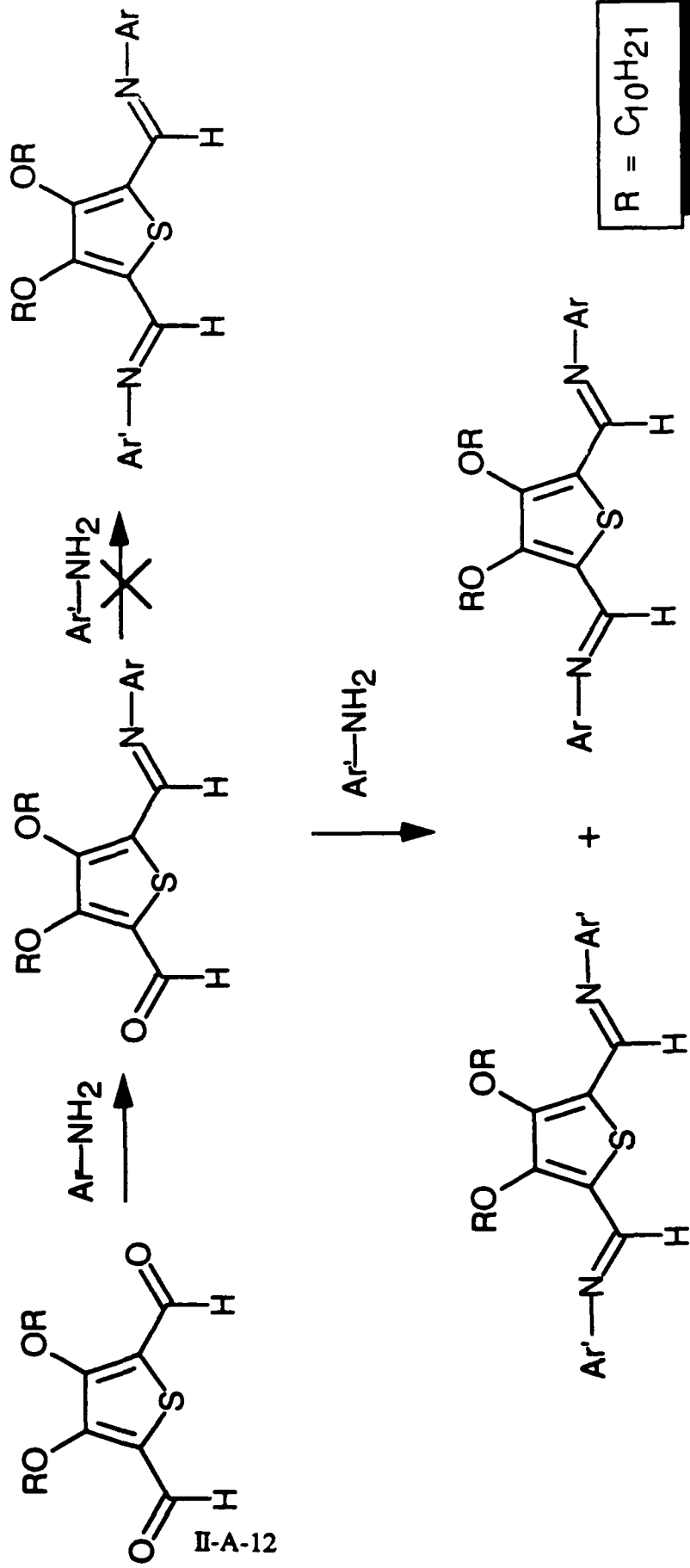
$\text{R} = \text{C}_{10}\text{H}_{21}$

Dialdehyde

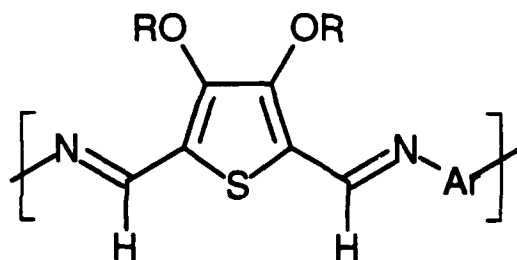


R = C₁₀H₂₁

Unsymmetrical Azomethines



Poly(thiophene azomethine)s

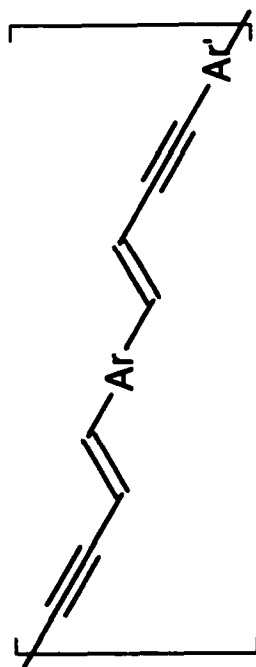


Ar	η_{inh} , dL/g 30°C	TGA Onset °C	Film Solvent	Color
	0.72 ^a	286	CH ₂ Cl ₂	bright red
	0.95 ^b	287	ØCH ₃ ^c	dark brown
	0.45 ^a	301	CH ₂ Cl ₂	orange
	0.16 ^a	282	CH ₂ Cl ₂	bright red

a) THF, conc. = 0.45 g/dL. b) MSA, conc. = 0.10 g/dL.

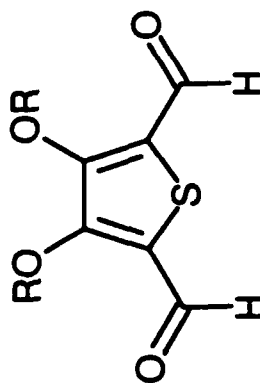
c) film was cast from reaction mixture and would not re-dissolve.

Thiophene Enynes

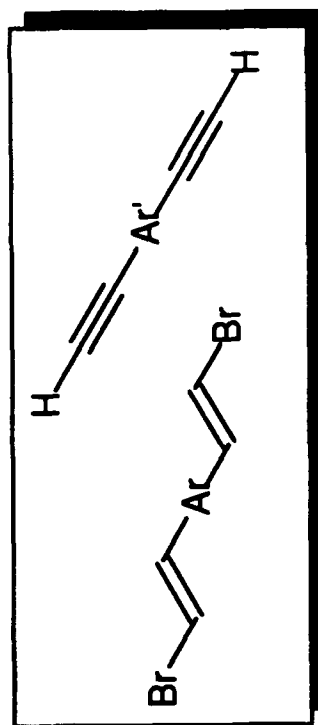


Compare to Diacetylene System

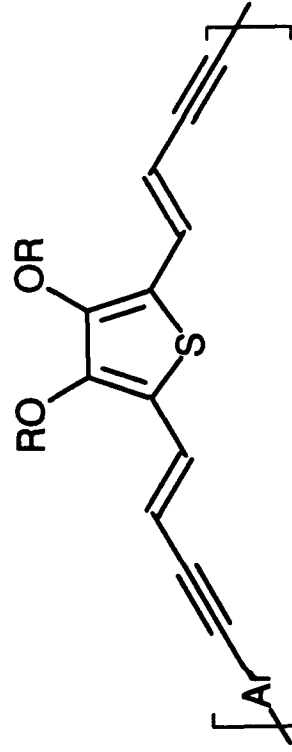
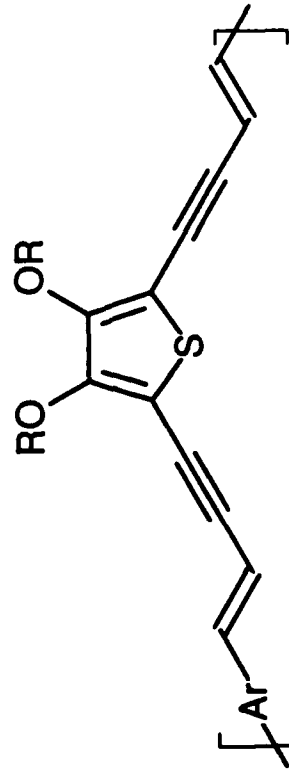
- Donor - Acceptor Ar



R = C₁₀H₂₁


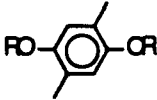







Enyne and Ynene Polymers



R = C₁₀H₂₁

Polythiophene Enynes and Ynenes

<i>Polythiophene Enyne^d</i> Ar =	Stereo-chemistry	$[\eta]^a$ dL/g	TGA Onset °C
	trans,trans	0.32	281 ^b
	trans,trans	0.90	325 ^b
	trans,trans	0.27	327 ^b
	trans,trans and cis, trans	0.74	328 ^b

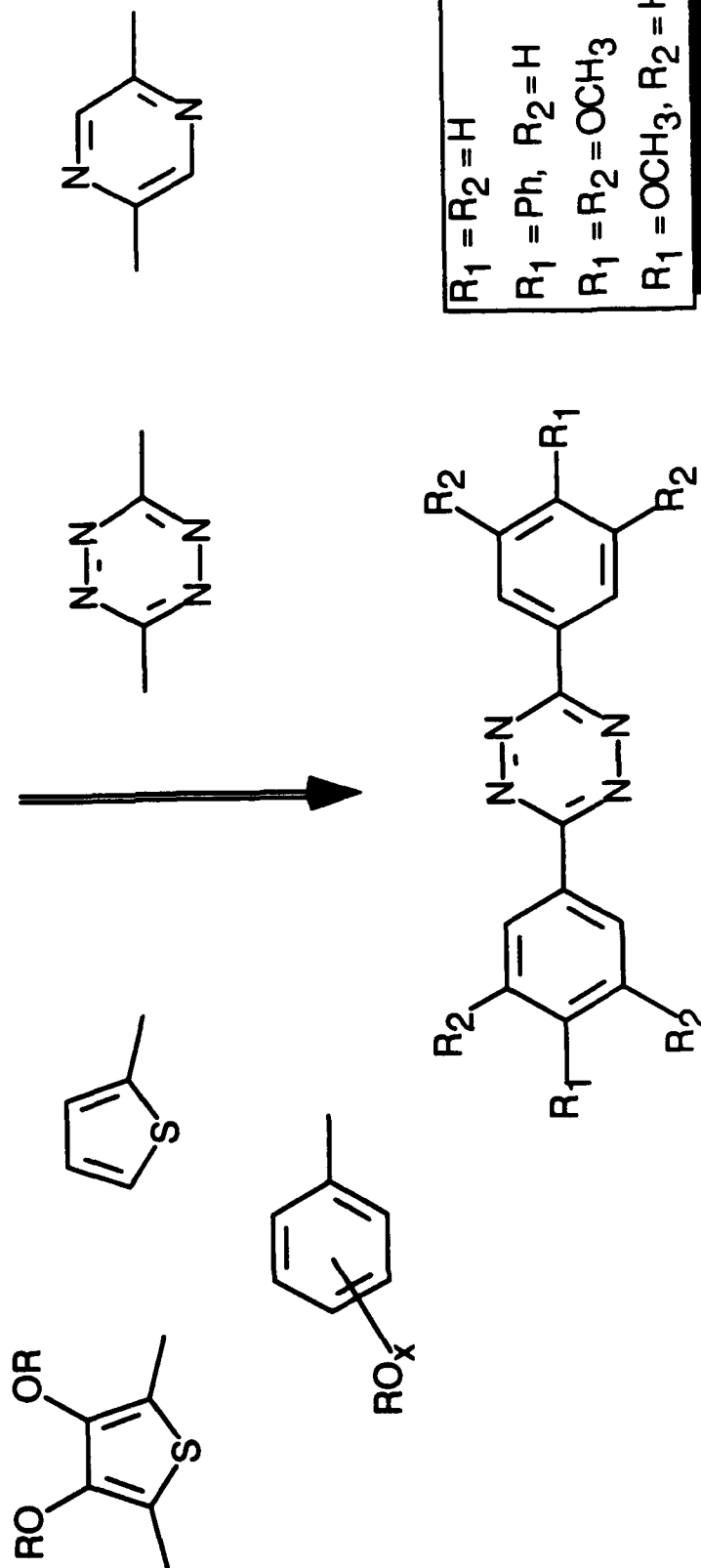
<i>Polythiophene Ynene^d</i> Ar =	Stereo-chemistry	$[\eta]^a$ dL/g	TGA Onset °C
	trans,trans	0.88	292 ^b
	trans,trans	0.72	275 ^b
	trans,trans	0.60	328 ^c

a) THF at 30°C. b) Run in N₂. c) Run in air.

d) Polymers would not re-dissolve in THF once dried.

Tetrazines / Pyrazines

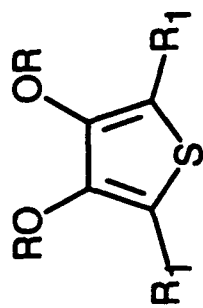
Donor D — A Acceptor



II-A-17

Unique Thiophene Donor Units

Solubilizing / Donor Function



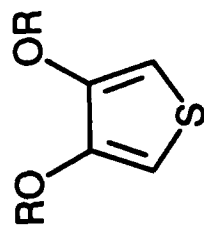
Linking Site - H, COOH, Hal

II-A-18

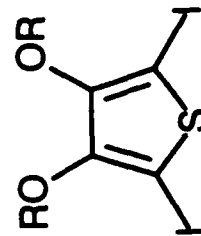
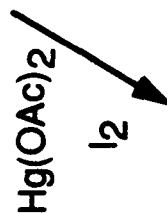
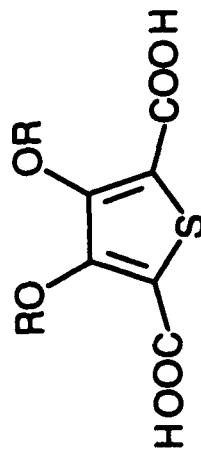
New Monomers and Model Components for:

- Enyne Synthesis
- Azomethine Synthesis
- Poly(thiophene)s

3,4-Dialkoxythiophenes



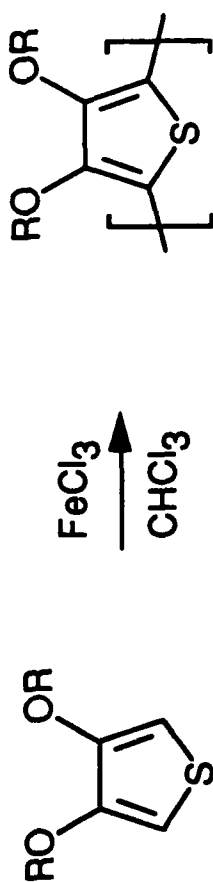
Heat



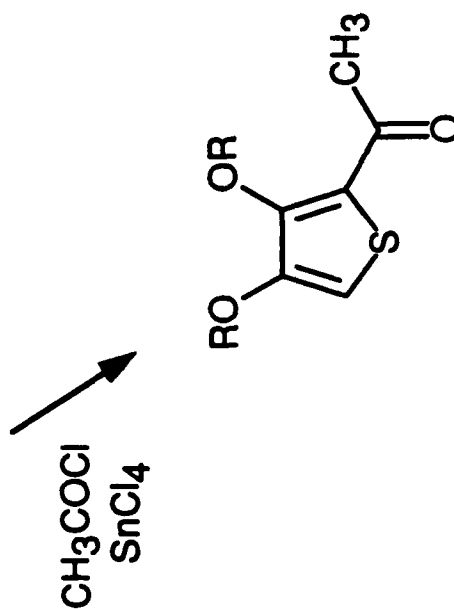
R	Yield	Mp(°C) / Bp (mm)
CH ₃	50 (q)	260-3 (0.2)
C ₄ H ₉	78 (m)	160-4 (0.2)
C ₁₀ H ₂₁	88 (m)	42-3
-CH ₂ CH ₂ -	54 (q)	65 (0.2)

m	Melt
q	Cu, Quinoline

Poly(3,4-dialkoxythiophene)s & Derivatives



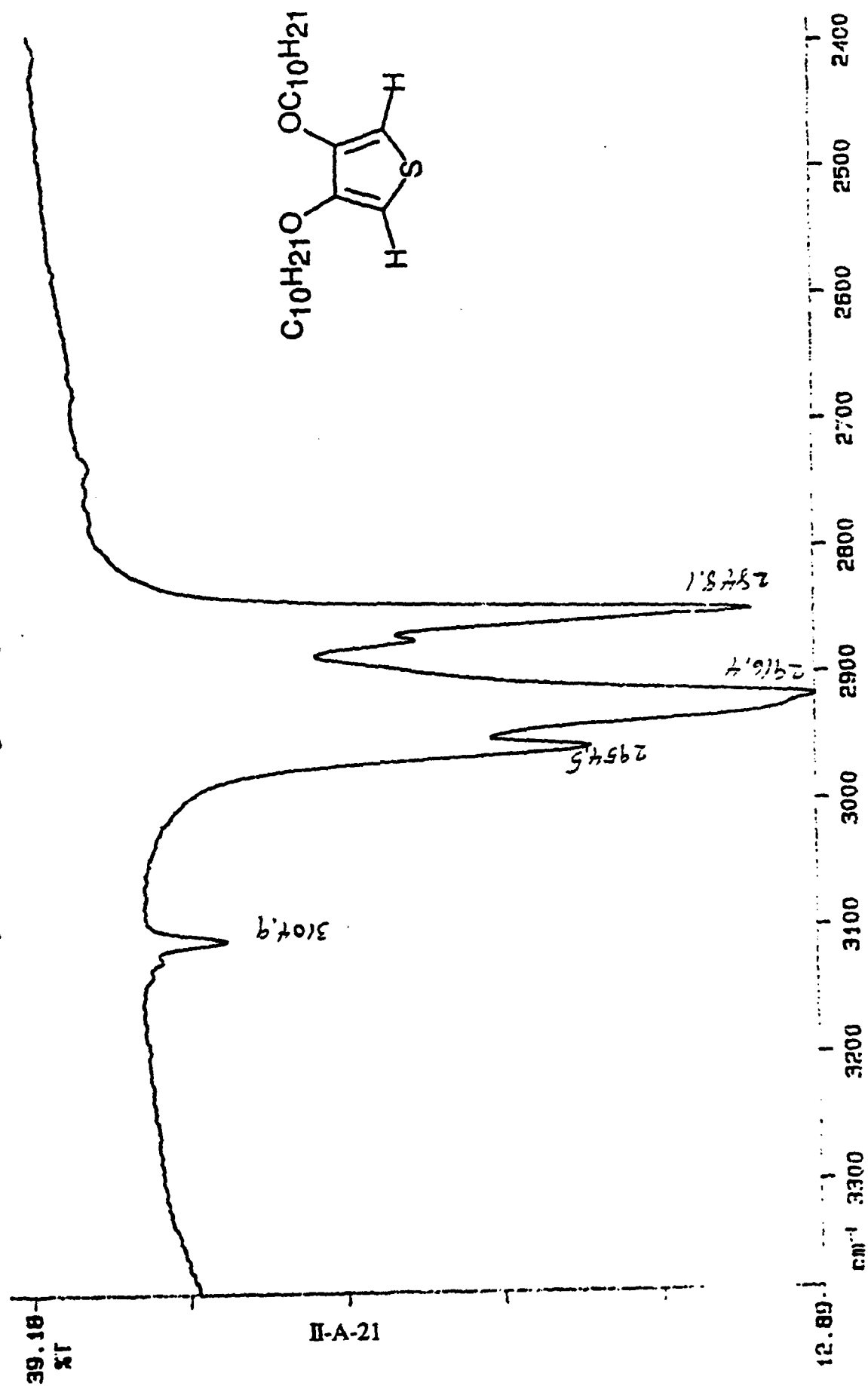
- Obtained as mixture of doped and undoped polythiophene
- Hydrazine Hydrate treatment



Department of Chemistry

Wright State University

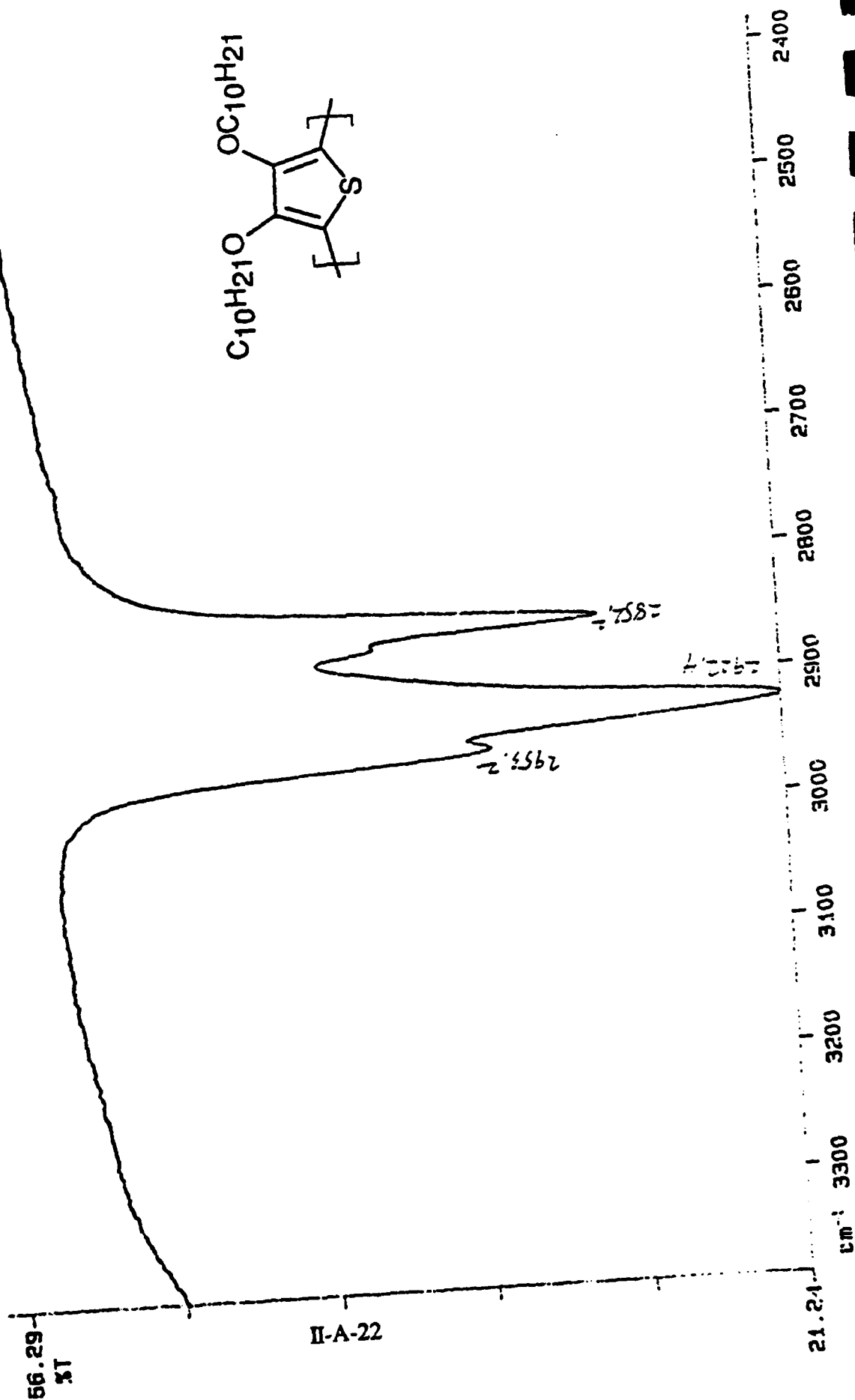
3,4-Didecyloxythiophene IR



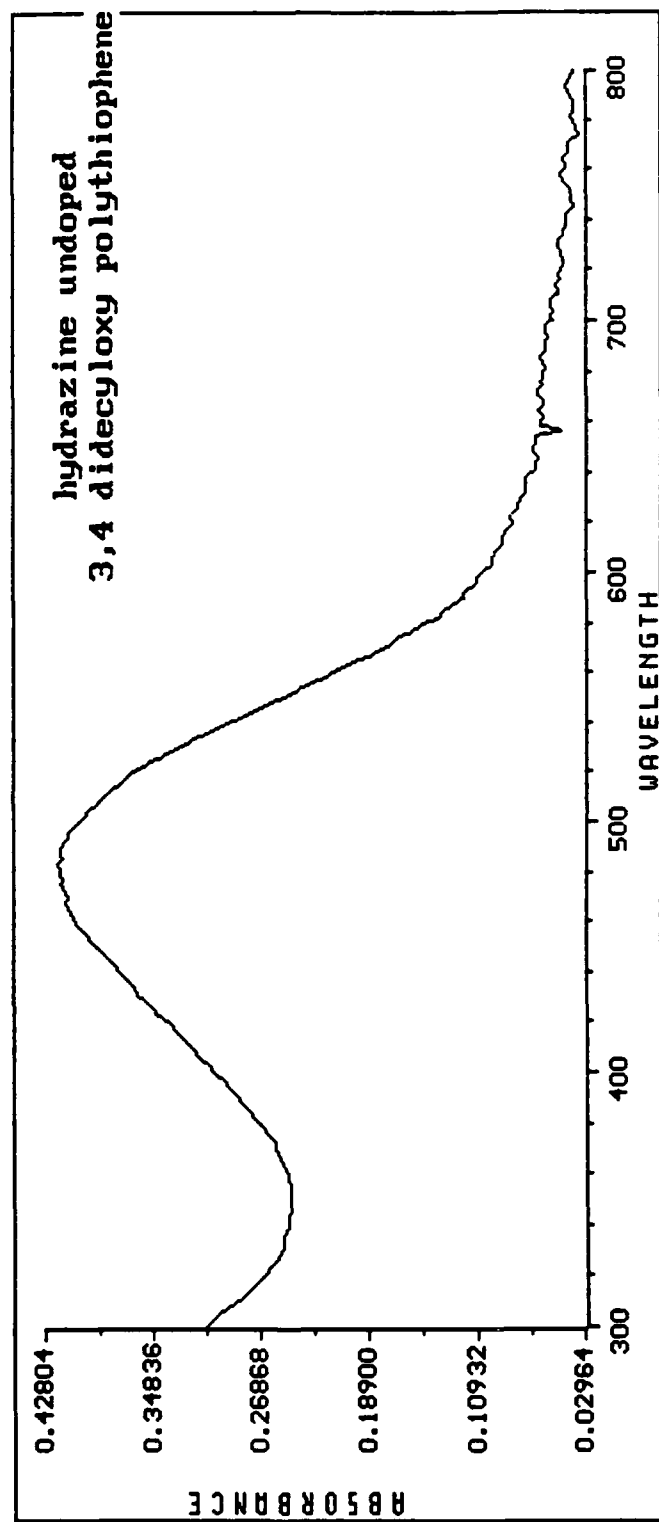
Department of Chemistry

Wright State University

Poly(3,4-didecyloxythiophene) IR



Poly(3,4-didecyloxythiophene) UV - VIS



II-A-23

Summary

- Thiophene-Azomethines
- Thiophene-Enynes
 - *Models and Polymers Synthesized and to be submitted for Chi(3) study*
- 3,4-Dialkoxythiophenes
 - *Alkoxy derivatives synthesized*
 - *Polymerized*
- Tetrazines
 - *Submitted for Chi(3) - Solubility?*

Acknowledgements

AFOSR

Dr. J.J. Kane Coinvestigator

Postdoctoral Associates:

Feng Gao
Savithri Krishnamurthy
Bob Miller
Rob McKellar

Masters Students:

K. Paulvannan
P. Bardwaj
M. Patel
J. Lin

Undergraduates:

Doug Bland
Mike Vier

NEW CHARACTERIZATION TECHNIQUES

Quasi-elastic Light Scattering

**} Transport in
Pores**

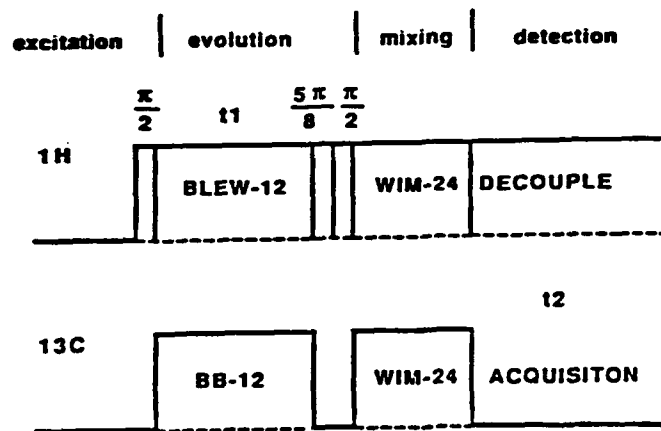
Forced Rayleigh Light Scattering

**Heteronuclear Correlation Two-Dimensional NMR
Spin Diffusion Techniques
Conformations; Ring Flips**

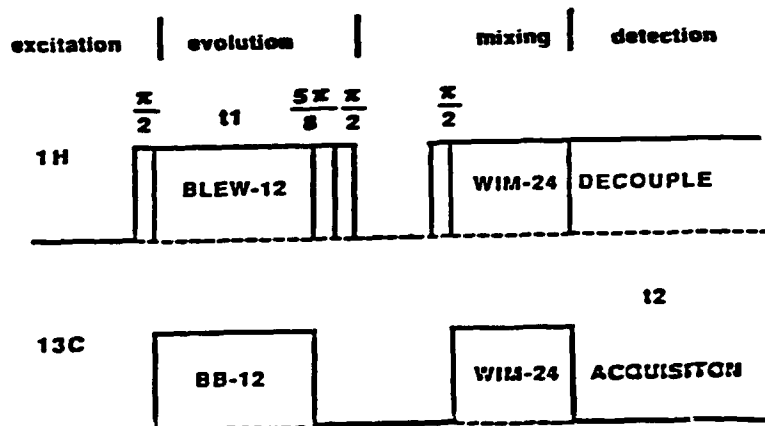
**Magnetic Effects on Polaron Generation in
Conjugated Systems**

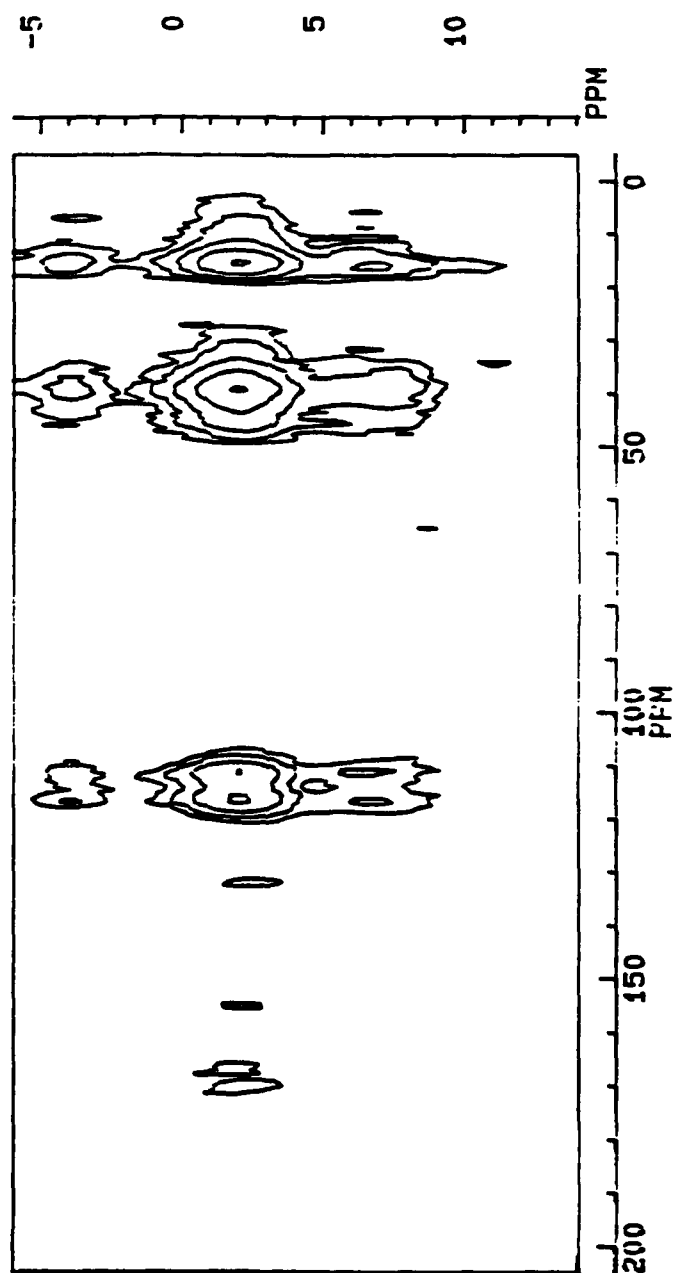
**Monte Carlo Simulations of Miscibility
Stiff Chains
Surfaces
Capillaries**

Pulse Sequence for Solid State HETCOR



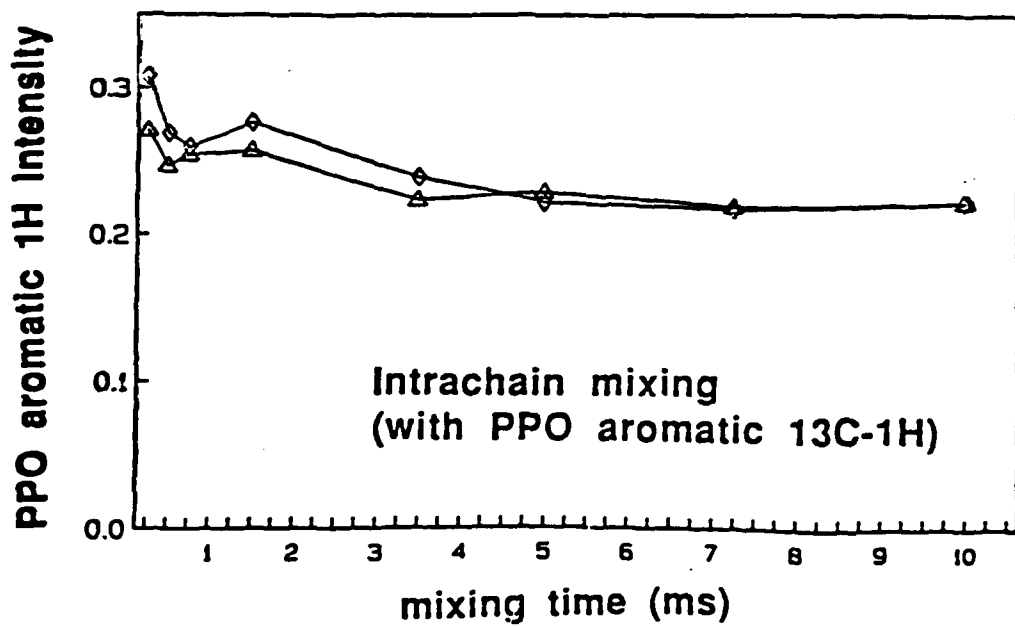
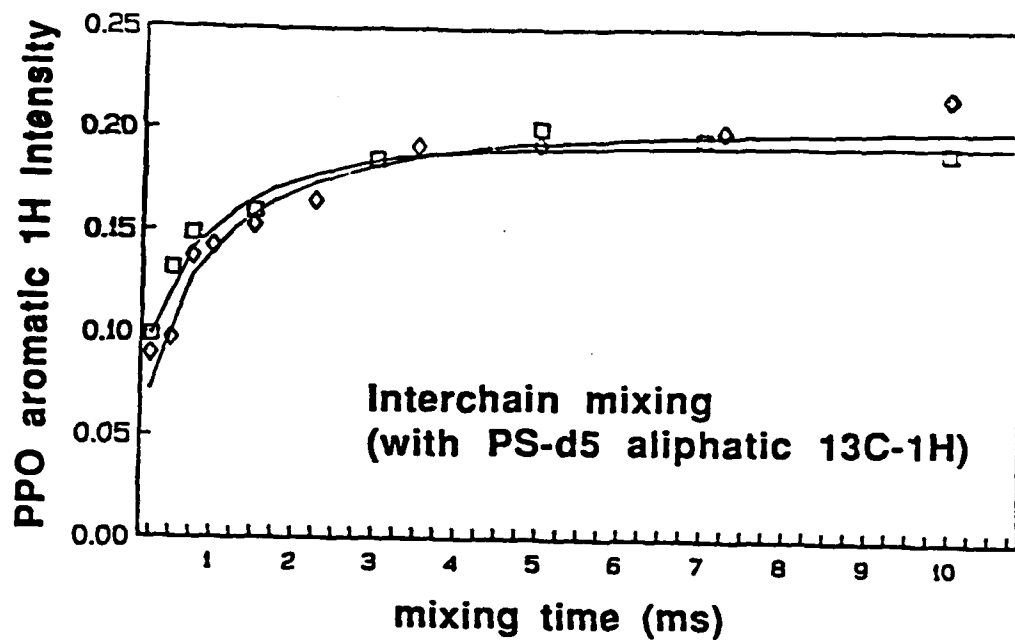
HETCOR with Spin Diffusion





II-A-28

Spin Diffusion Mixing of PPO/PS-d5 (50/50)



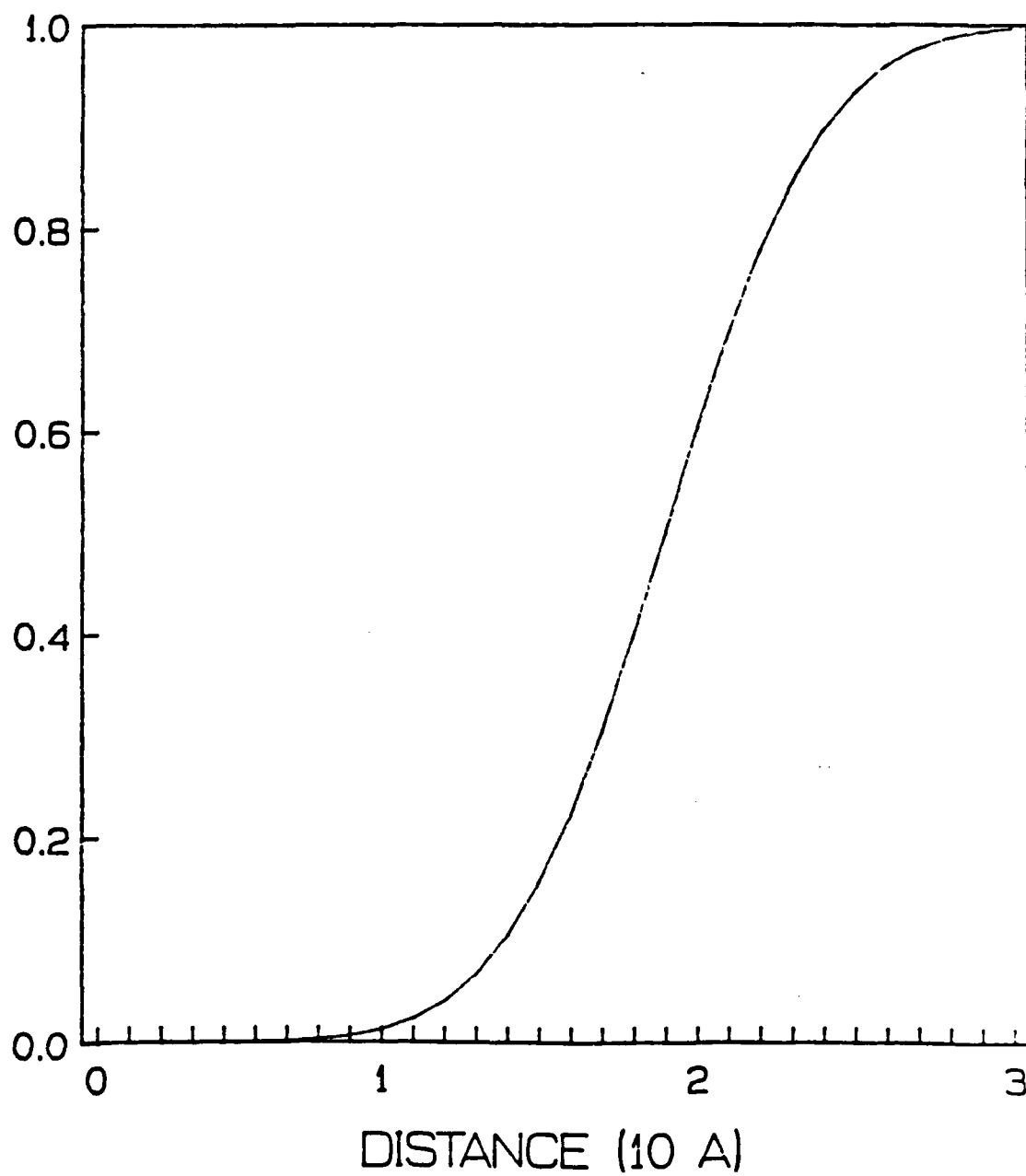
Calculation of Cross-peak Build-up Curves

1. Solve the diffusion equation for a particular model of "domain shape" (present method requires assumption of a cubic domain structure).
2. Calculate the radial pair correlation function between segments of the two chains (relate the result of a Monte-Carlo calculation to an NMR measurement).

Spin Diffusion ($r > 3.0 \text{ \AA}$)

$$r(\text{\AA}) = (60,000.0 \cdot t)^{1/2}$$

$$r = (6Dt)^{1/2} \quad D = 10^4 \text{ \AA}^2/\text{s}$$



II-A-31

INTERCHAIN CONTACTS IN A COMPATIBLE MIXTURE (PPO/PS-d5)

1. How many contacts per chain?
2. Is the interaction associated with a specific segmental conformation?

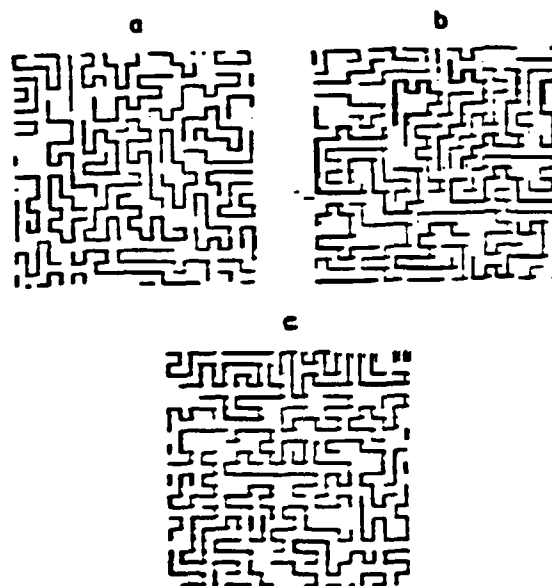
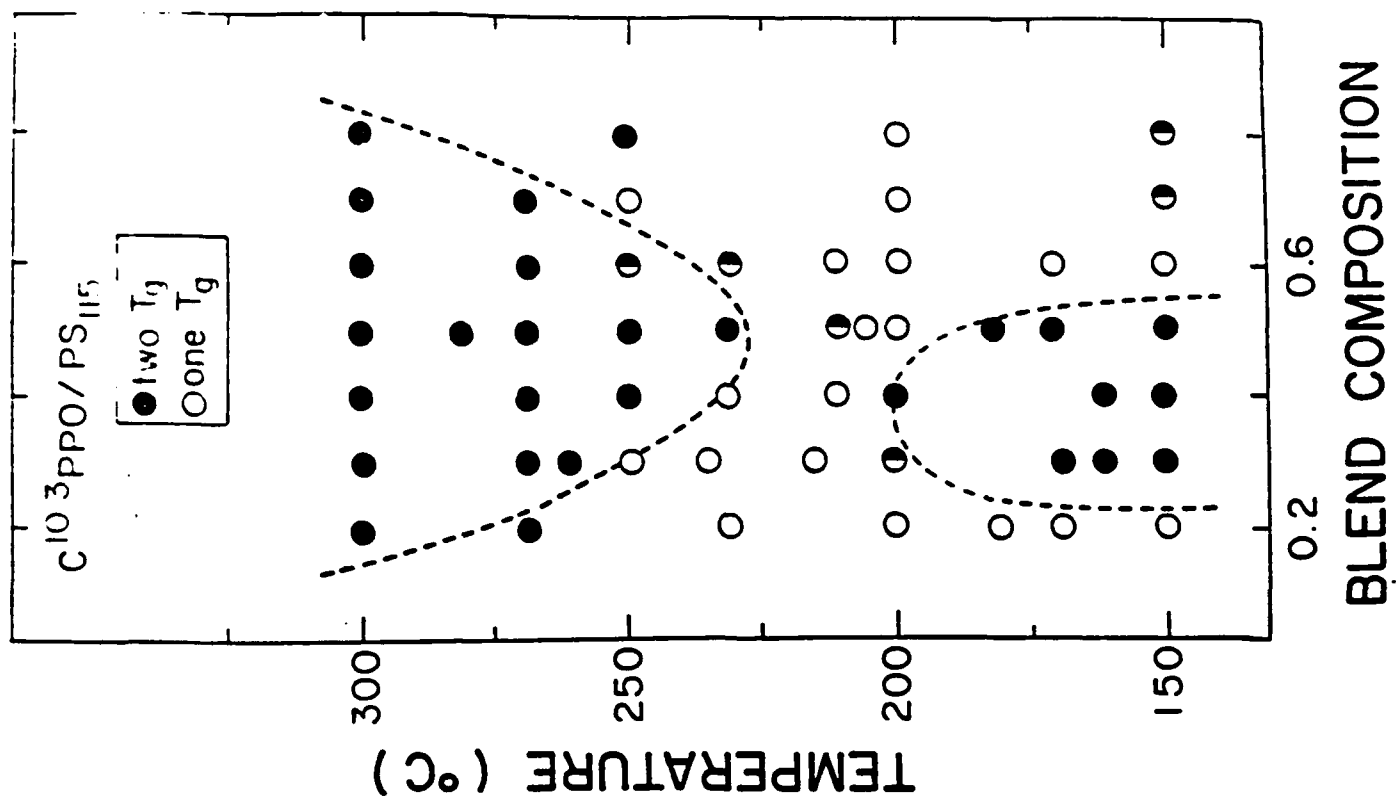
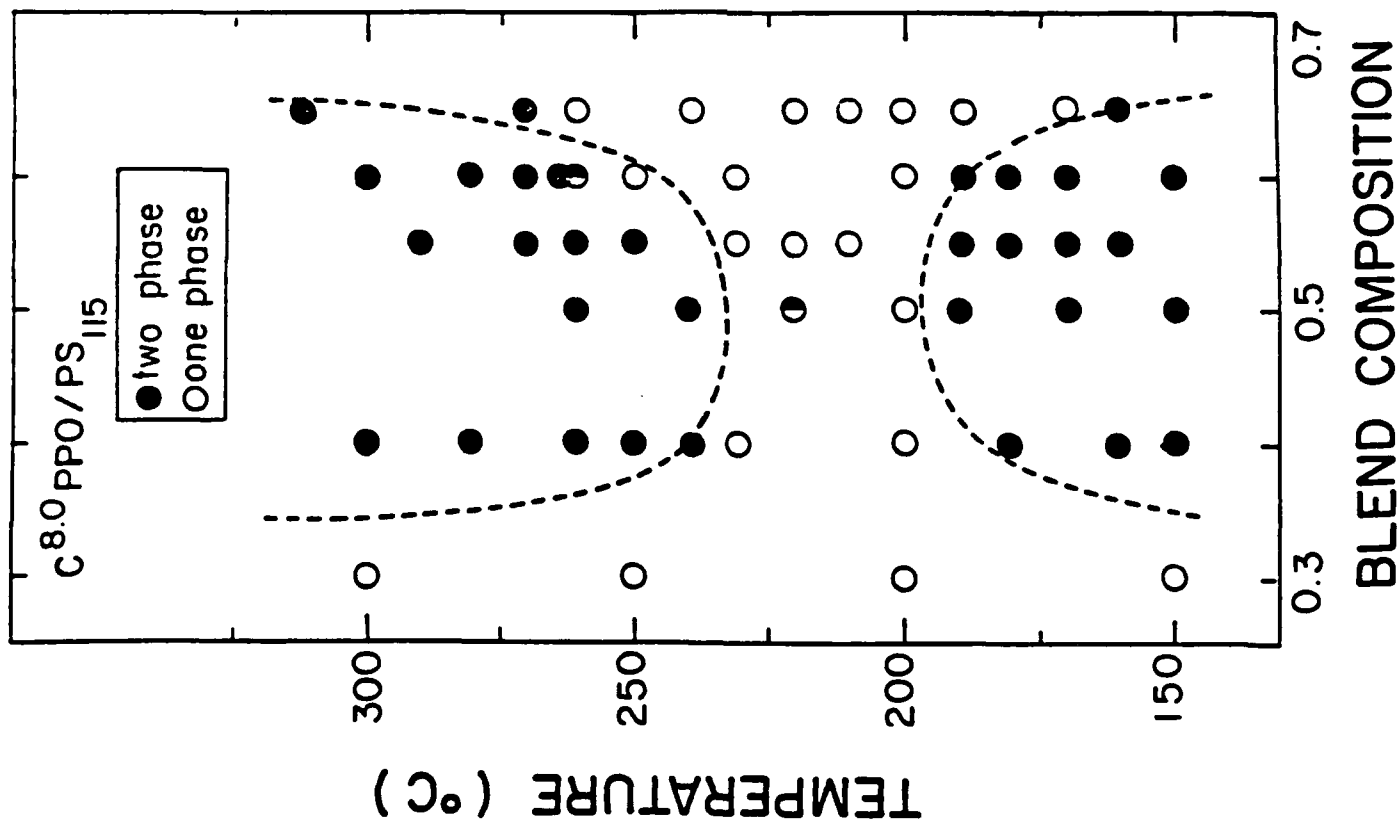


Figure 2. Snapshot picture of the mixture corresponding to three states on the transition curve shown in Figure 1: a, $\chi = 0$; b, $\chi = -0.5$; c, $\chi = 0.5$, representing athermal, miscible, and immiscible regimes and taken after a long equilibration time.

Cifra et al, Macromolecules 1988, 21, 446



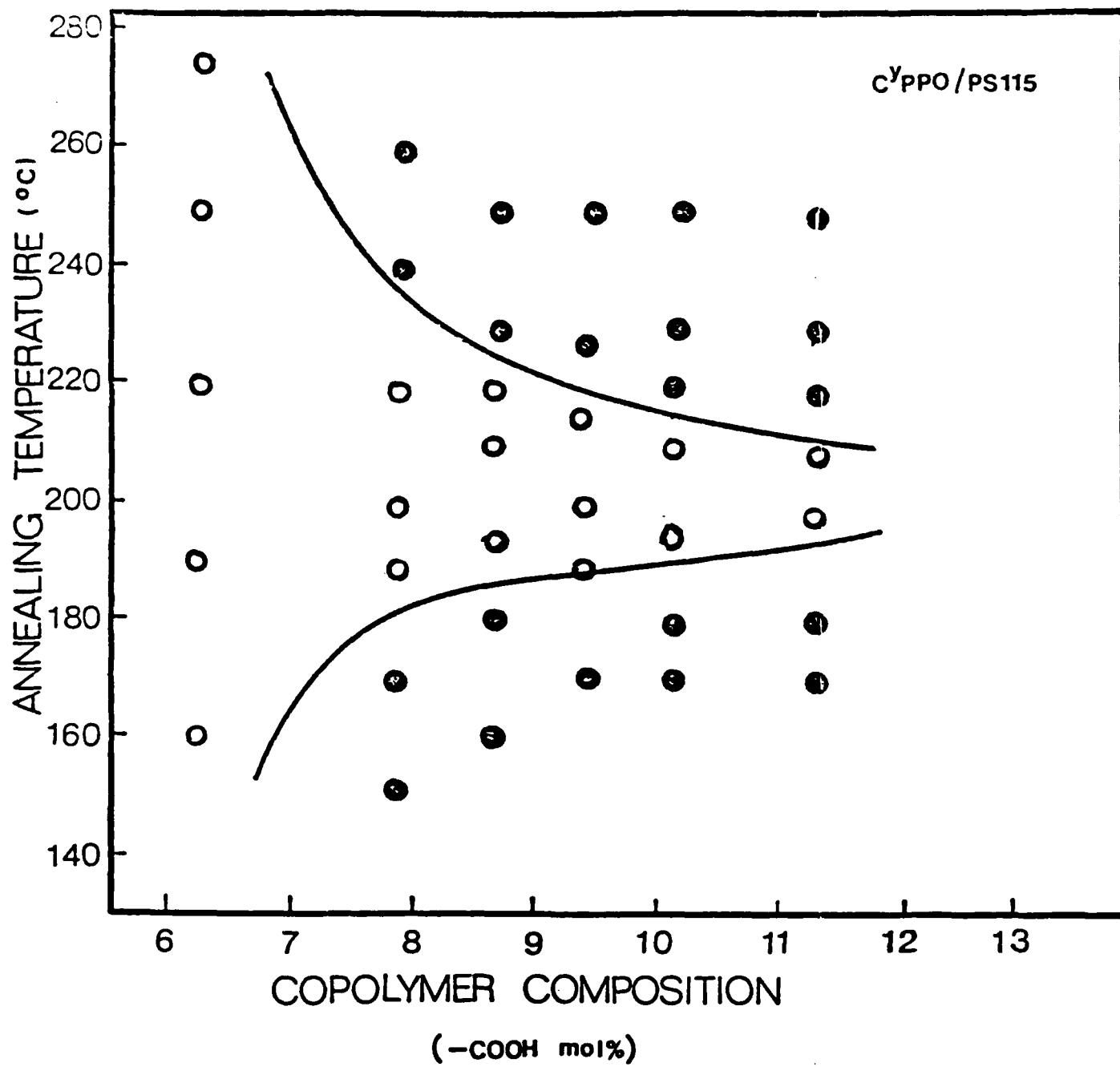
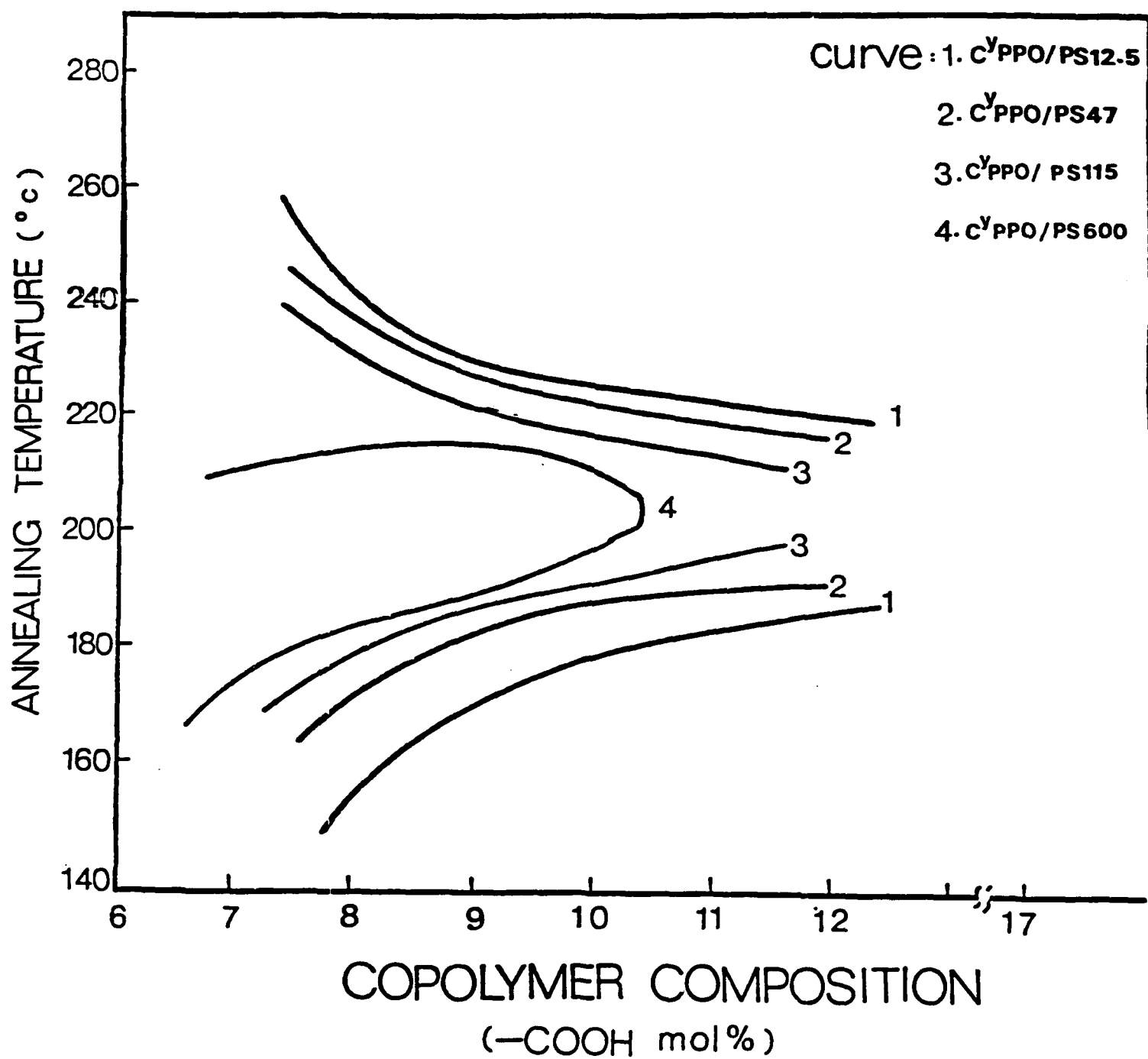


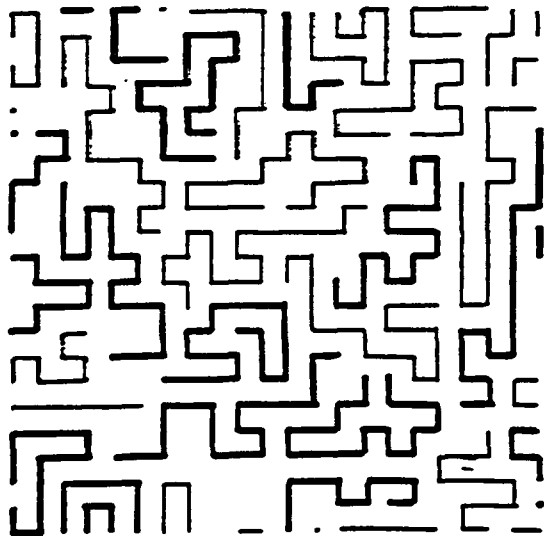
Fig. 6



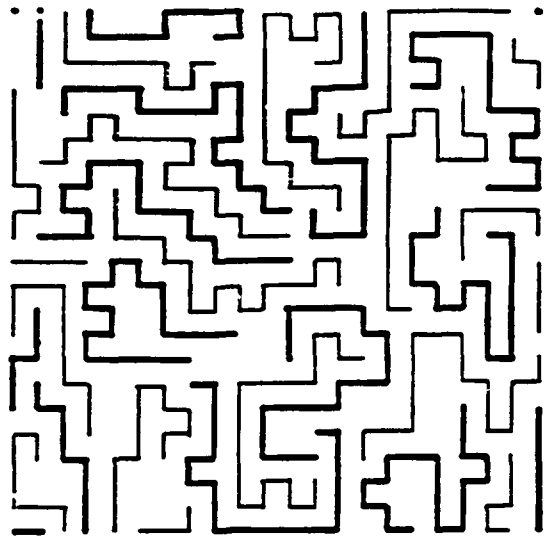
2D

$\epsilon' = 0$

a

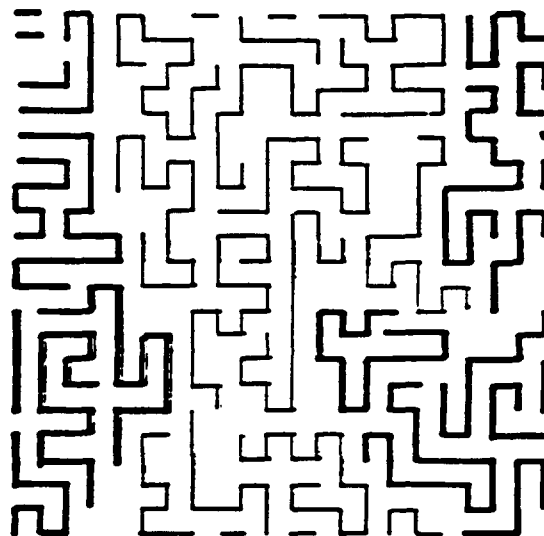


b



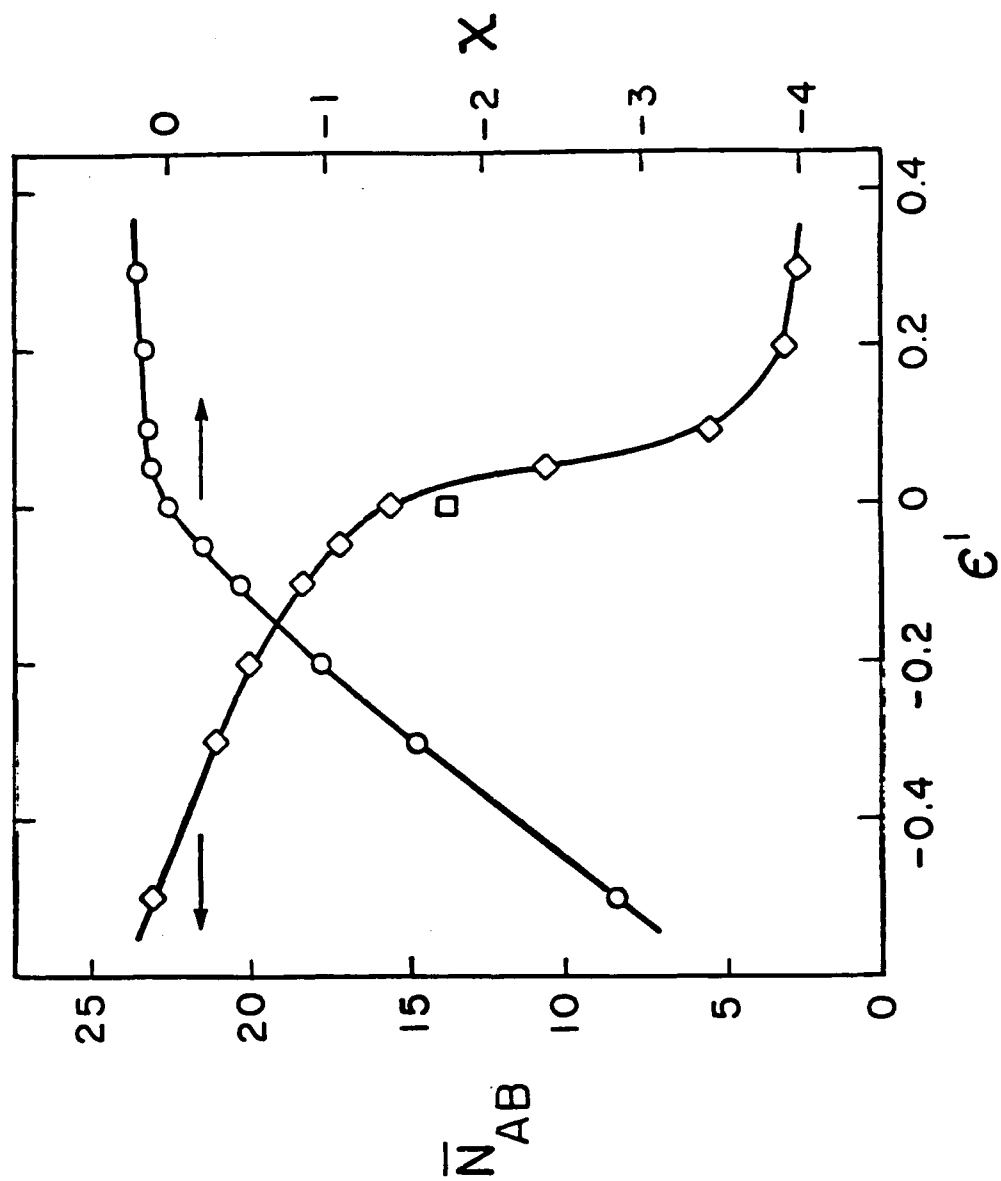
$\epsilon' = 0.5$

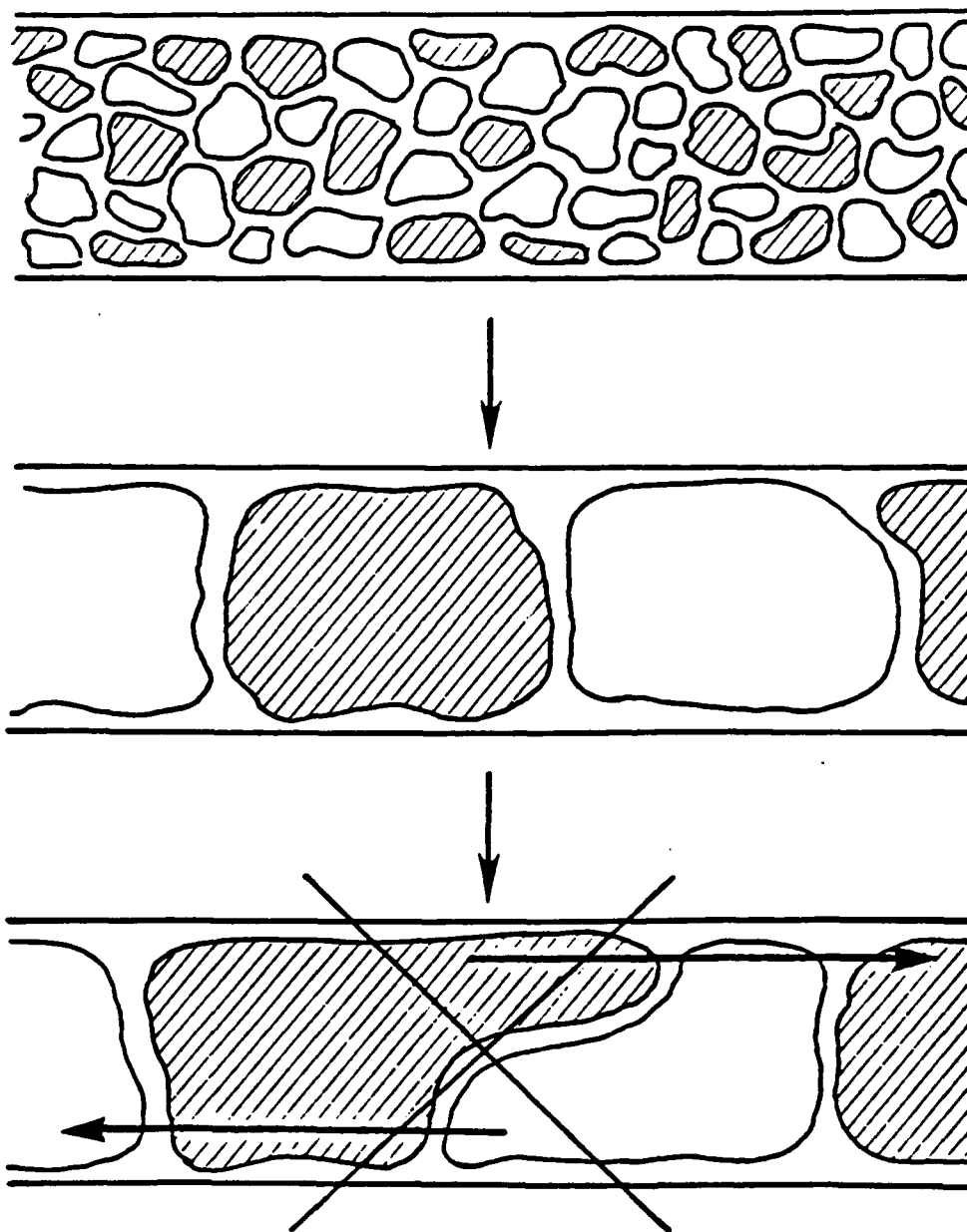
c



$\epsilon' = 10.5$

31



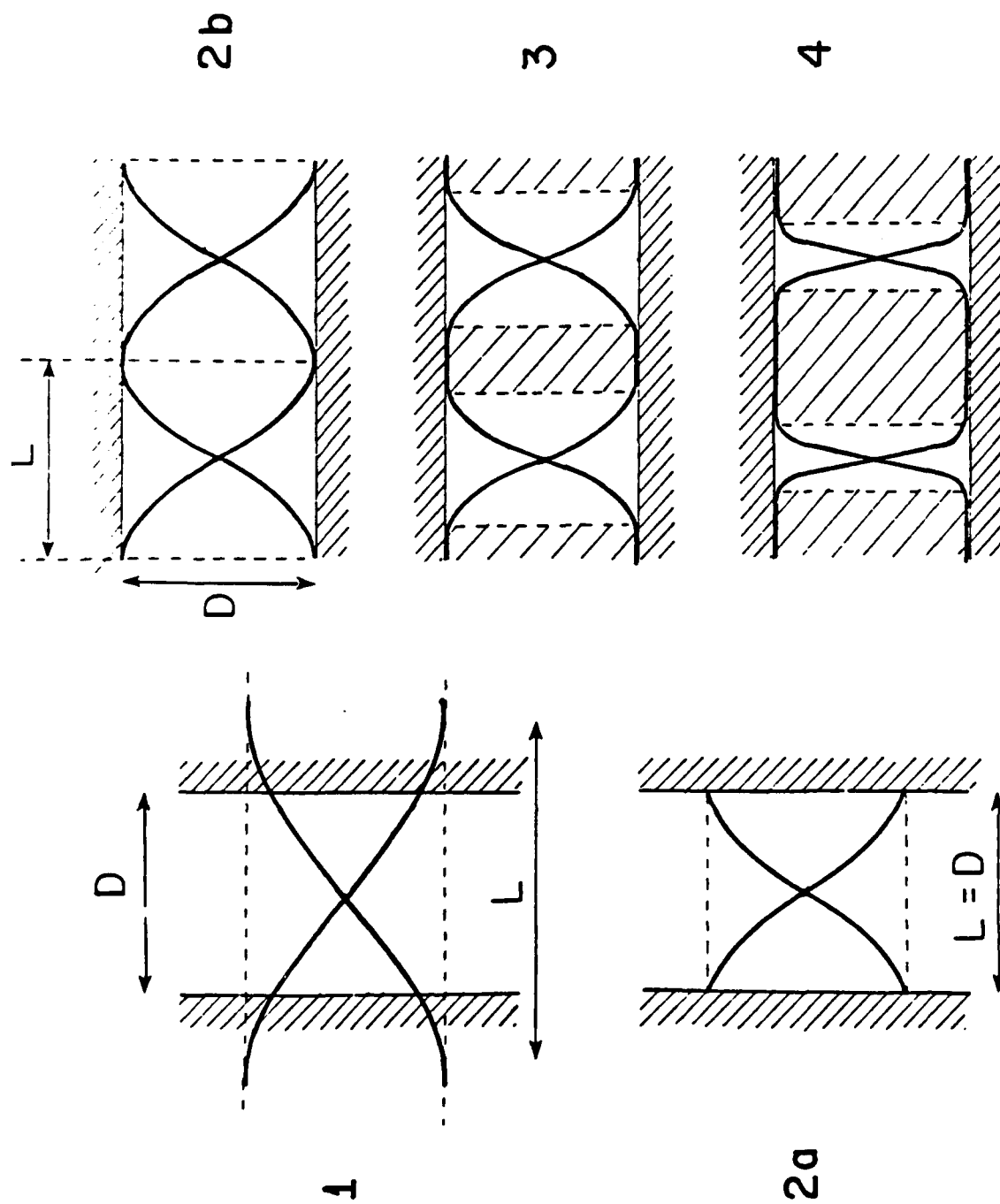


P. Cifra et al.
"Polymer miscibility..."

Figure 1

Figure 1

II-A-38



II-A-39

Figure 2

P. Cifra et al.
"Polymer miscibility..."

Figure 2

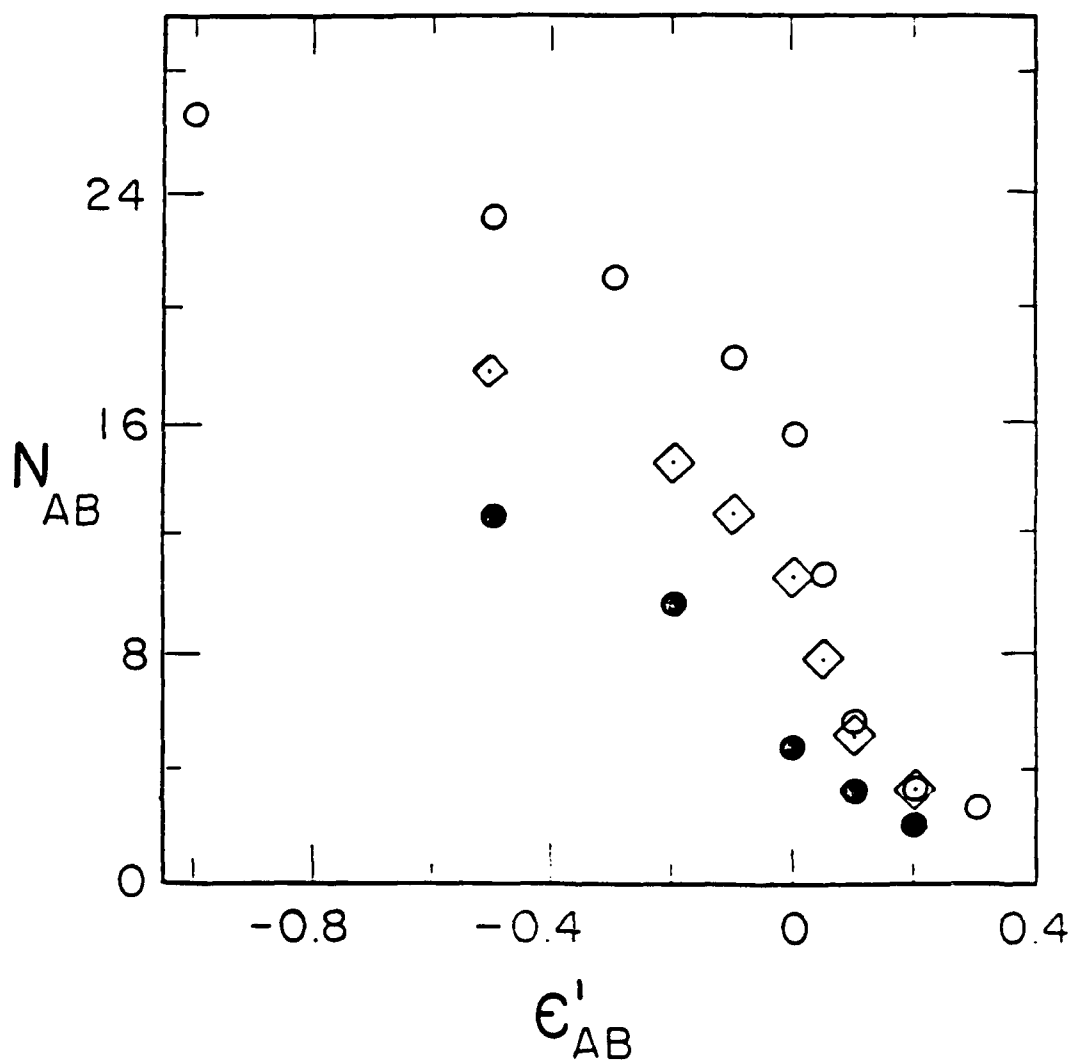
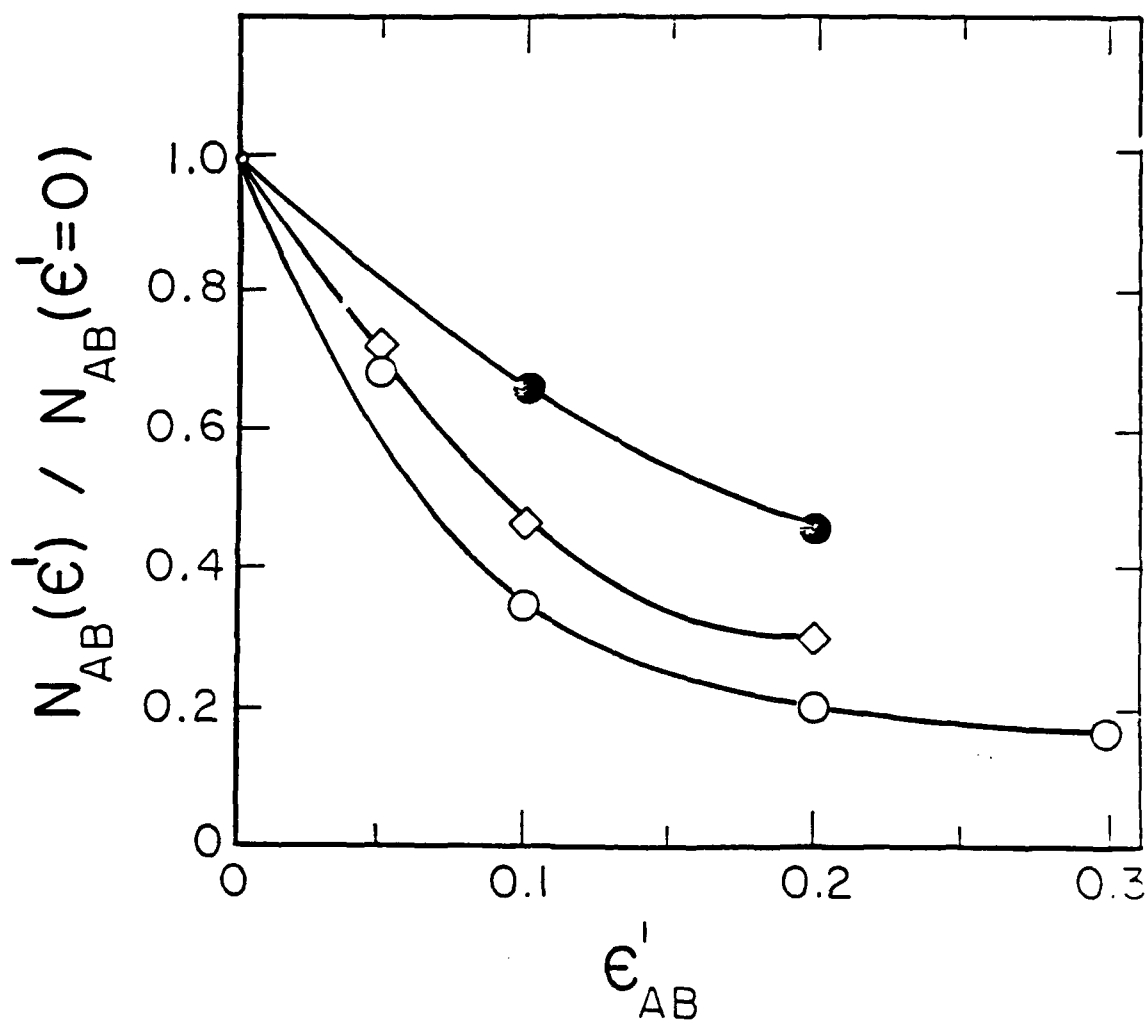


Figure 3

II-A-40

P. Cifra et al.
"Polymer miscibility..."

Figure 3



II-A-41

P. Cifra et al.
"Polymer miscibility..."

Figure 4

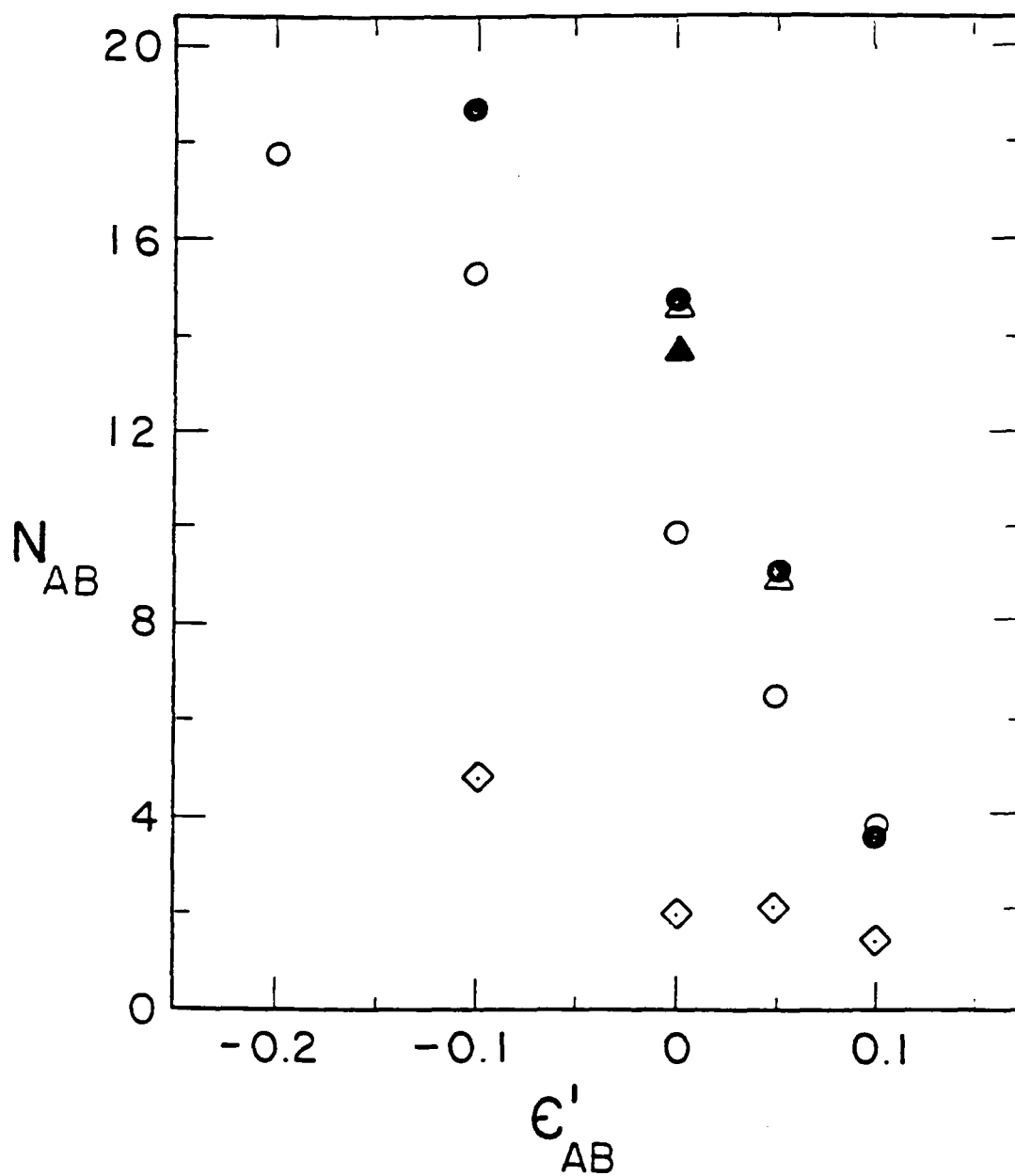
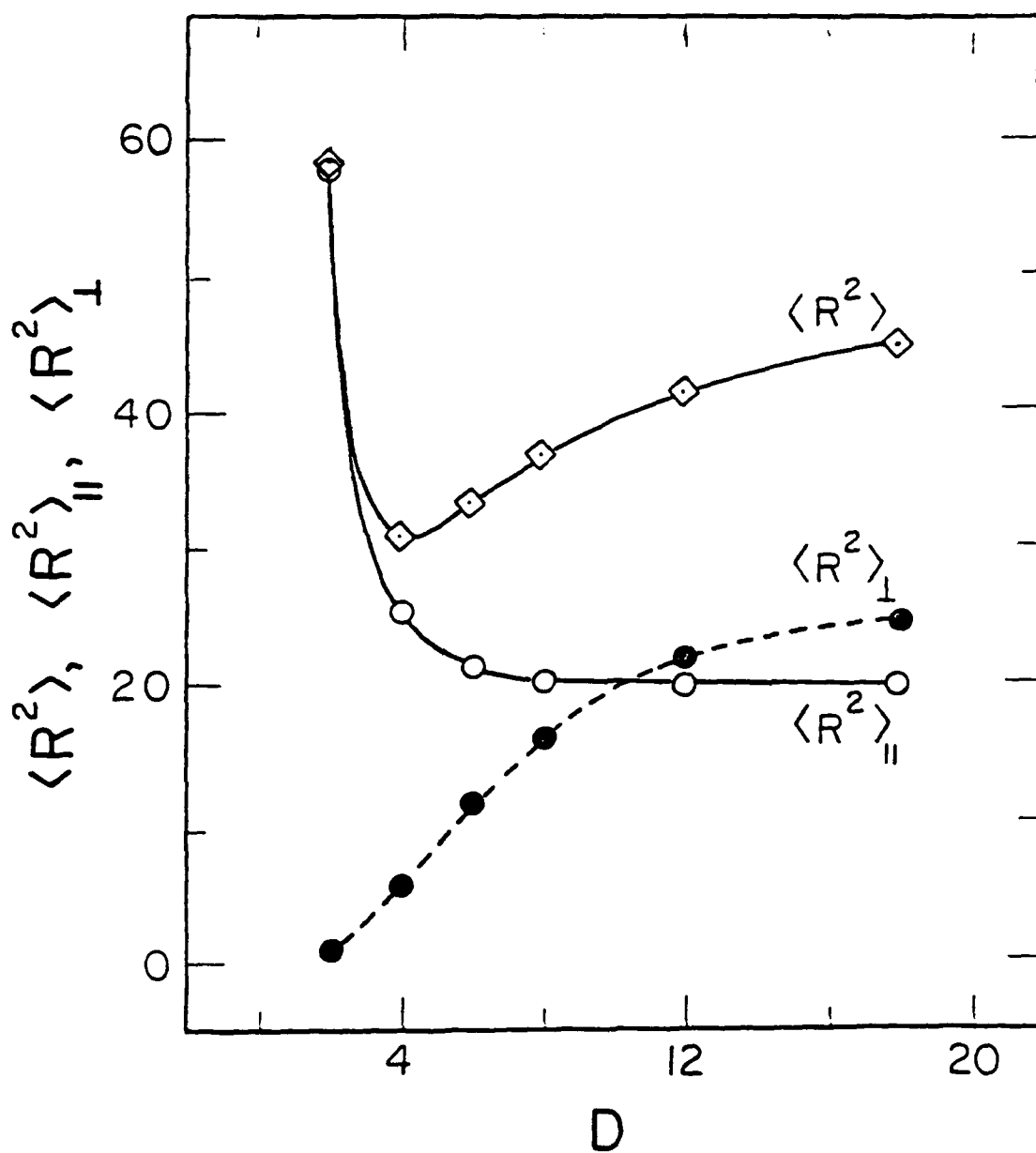


Figure 5

II-A-42

P. Cifra et al.
"Polymer miscibility..."

Figure 5



II-A-43

Figure 6

P. Cifra et al.
"Polymer miscibility..."

Figure 6

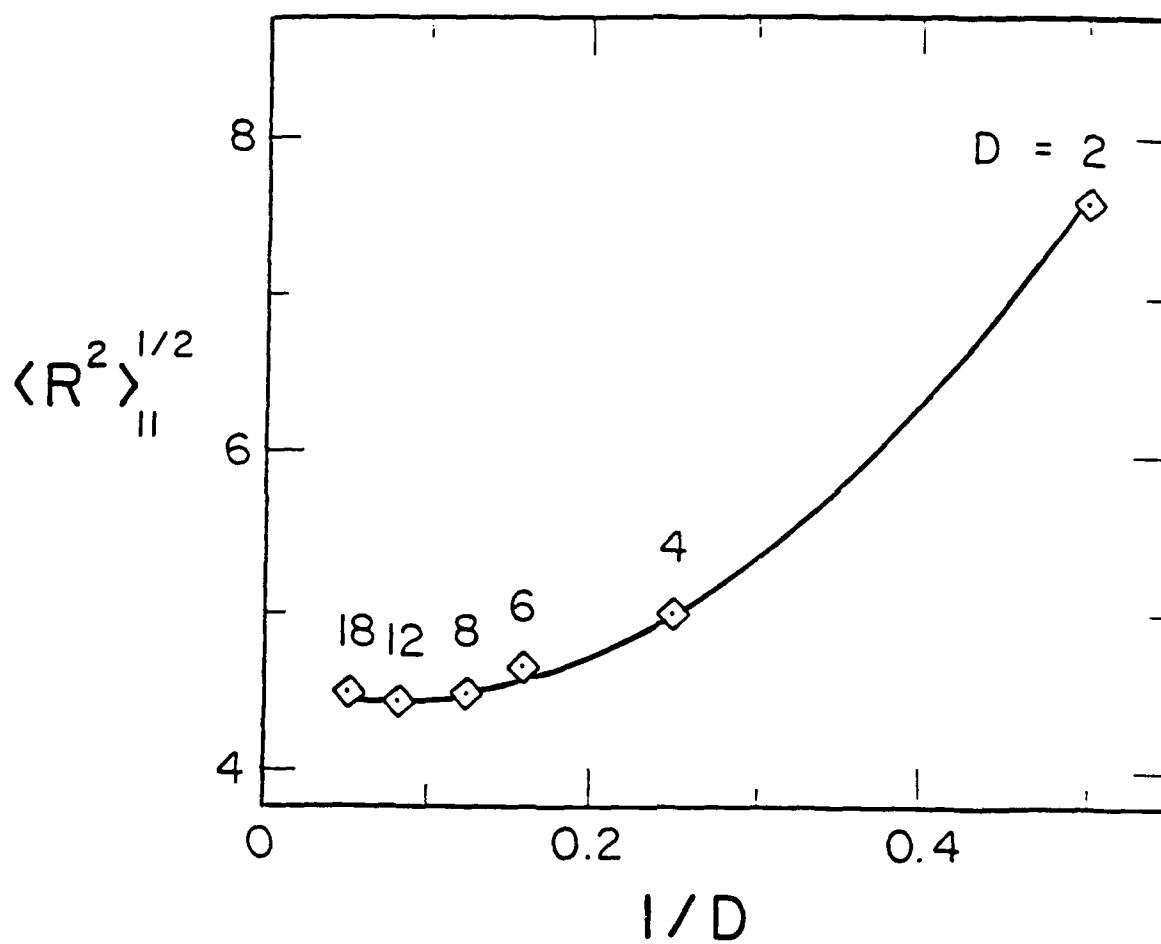


Figure 7

II-A-44

P. Cifra et al.
"Polymer miscibility..."

Figure 7

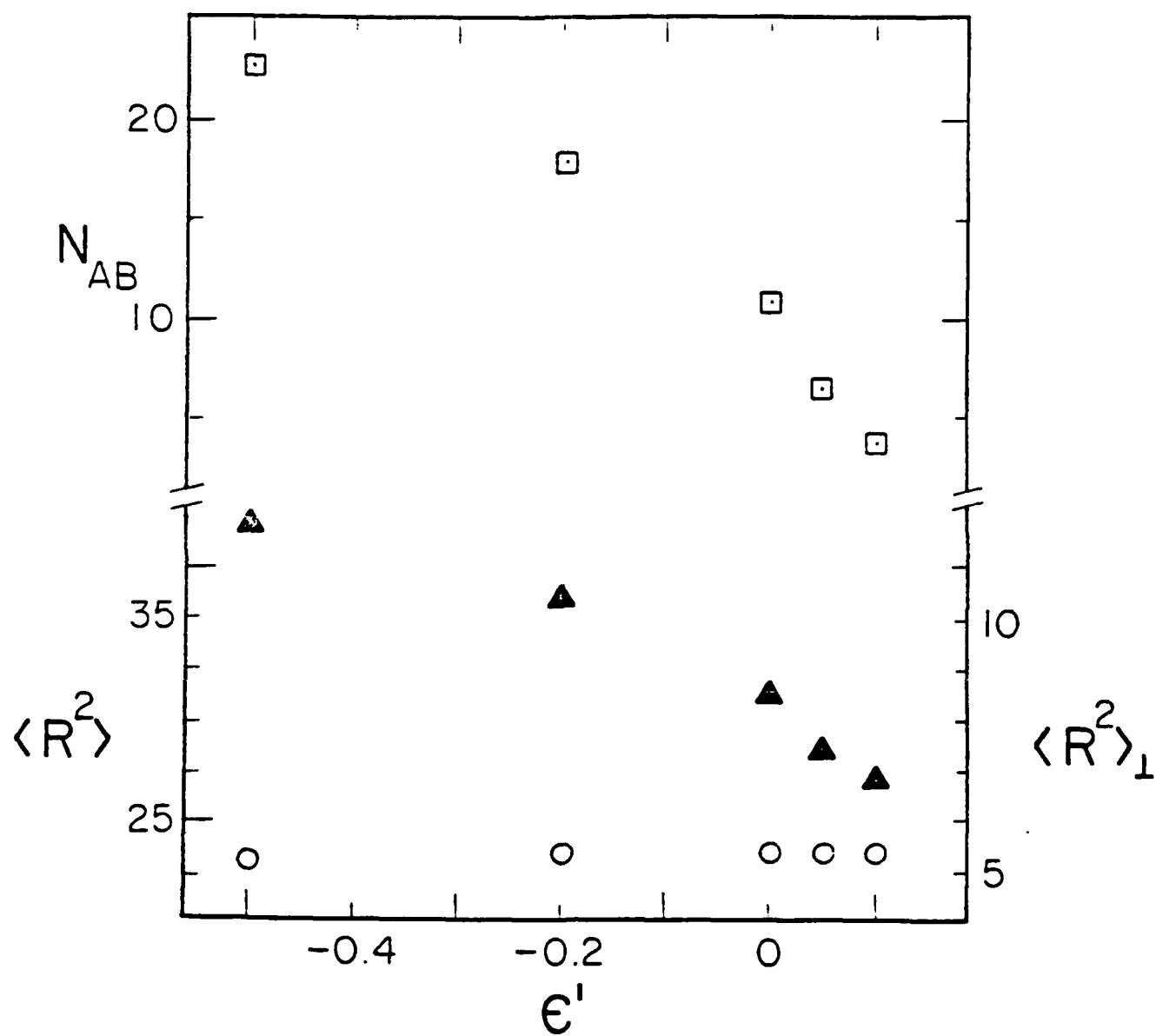


Figure 9

II-A-45

P. Cifra et al.
"Polymer miscibility..."

Figure 9

DARPA REVIEW

Kent G. Blizzard
Mark A. Druy

Foster-Miller, Inc.
350 Second Avenue
Waltham, MA 02154-1196

January 14, 1992

II-A-46

ULTRAHIGH PERFORMANCE POLYMER BLENDS

- Goals
 - To develop new processing capabilities for polymer systems for use at 300° to 400°C
- Accomplishments
 - Develop solution techniques to prepare single phase systems
 - Developed melt processing techniques for production of
 - Films
 - Rods
 - Sheet
 - Composites

II-A-47

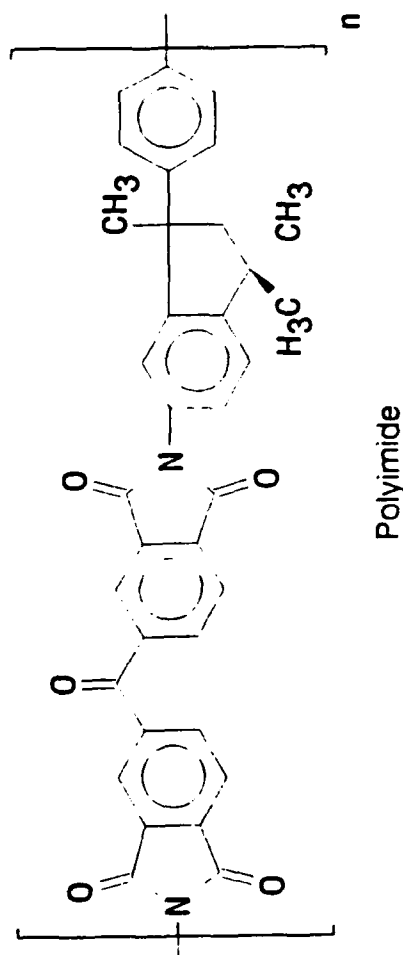
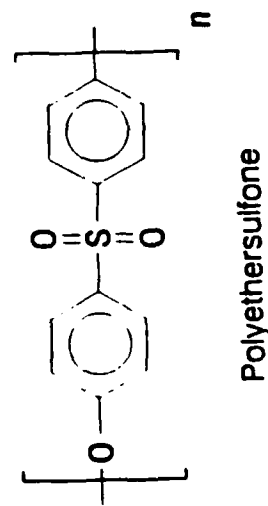
MATERIALS

- Blends of polyimides and polyethersulfone

- Tg PES:
230°C

- Tg PI: 323°

II-A-48



POLYIMIDE/PES BLEND MELT PROCESSING

II-A-49

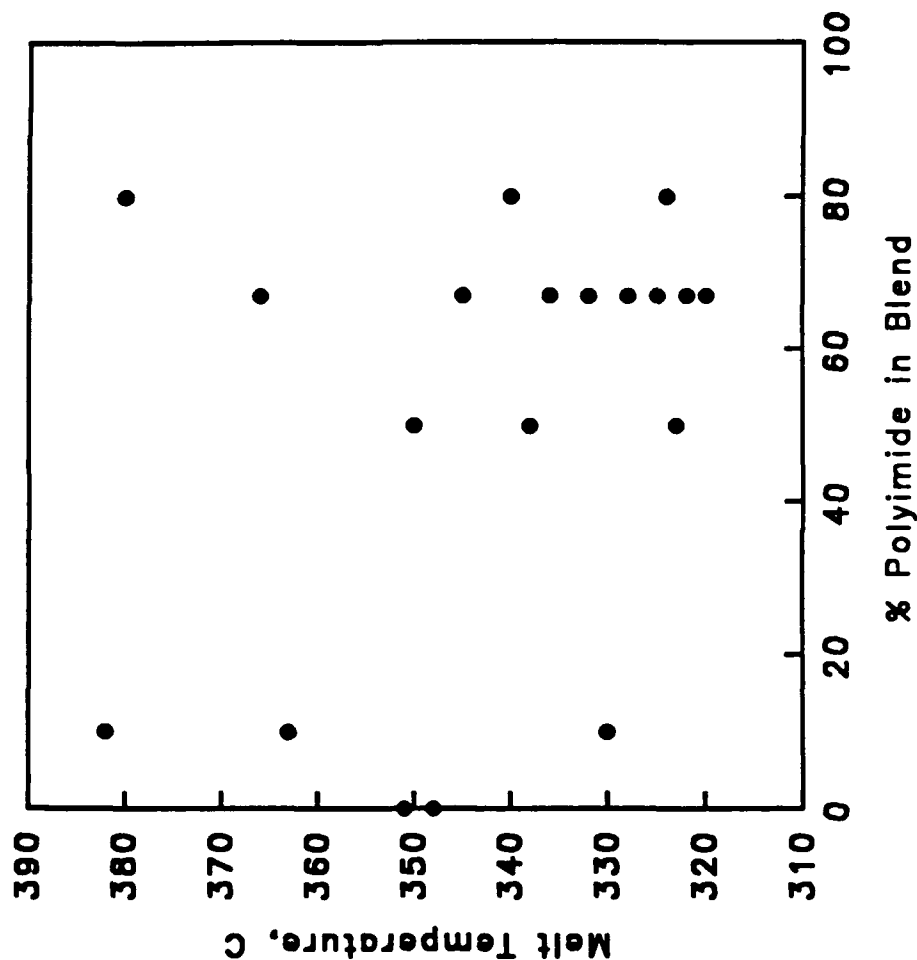
- Component rheology
- Blend mixing analysis in torque rheometer
- Scale up to 25 mm twin screw extruder

BLEND MELT PROCESSING CONSIDERATIONS

II-A-50

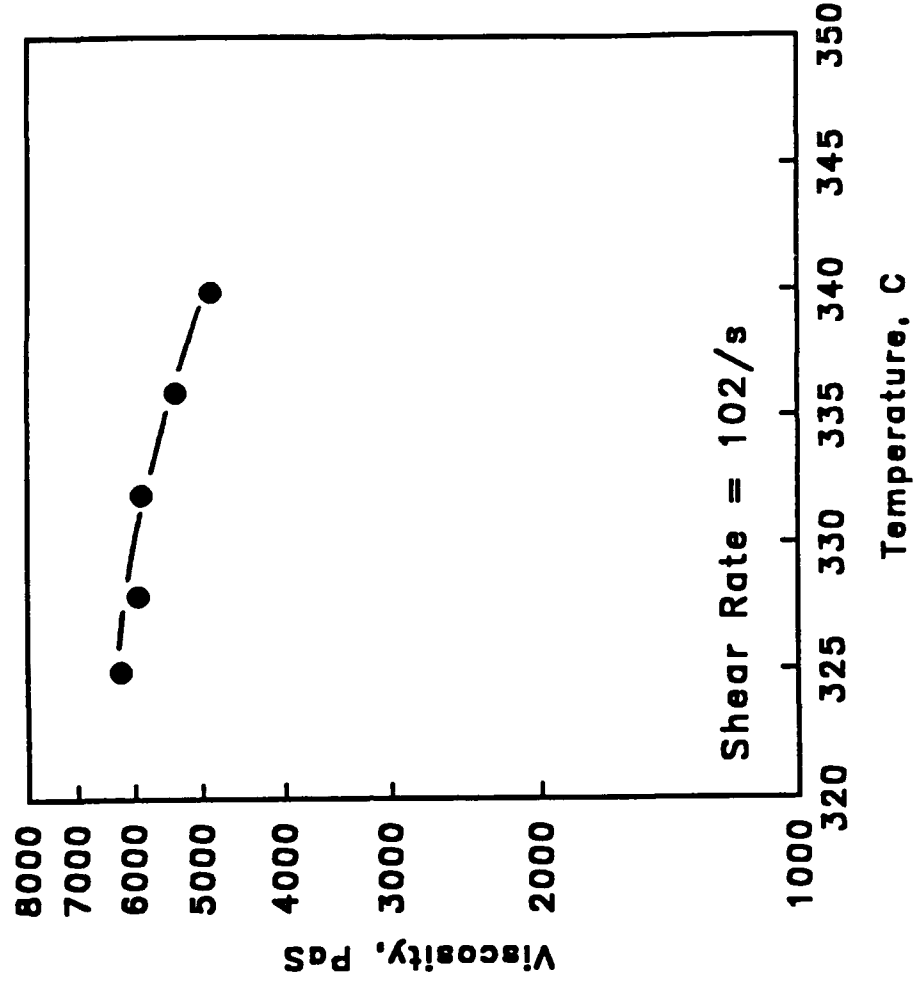
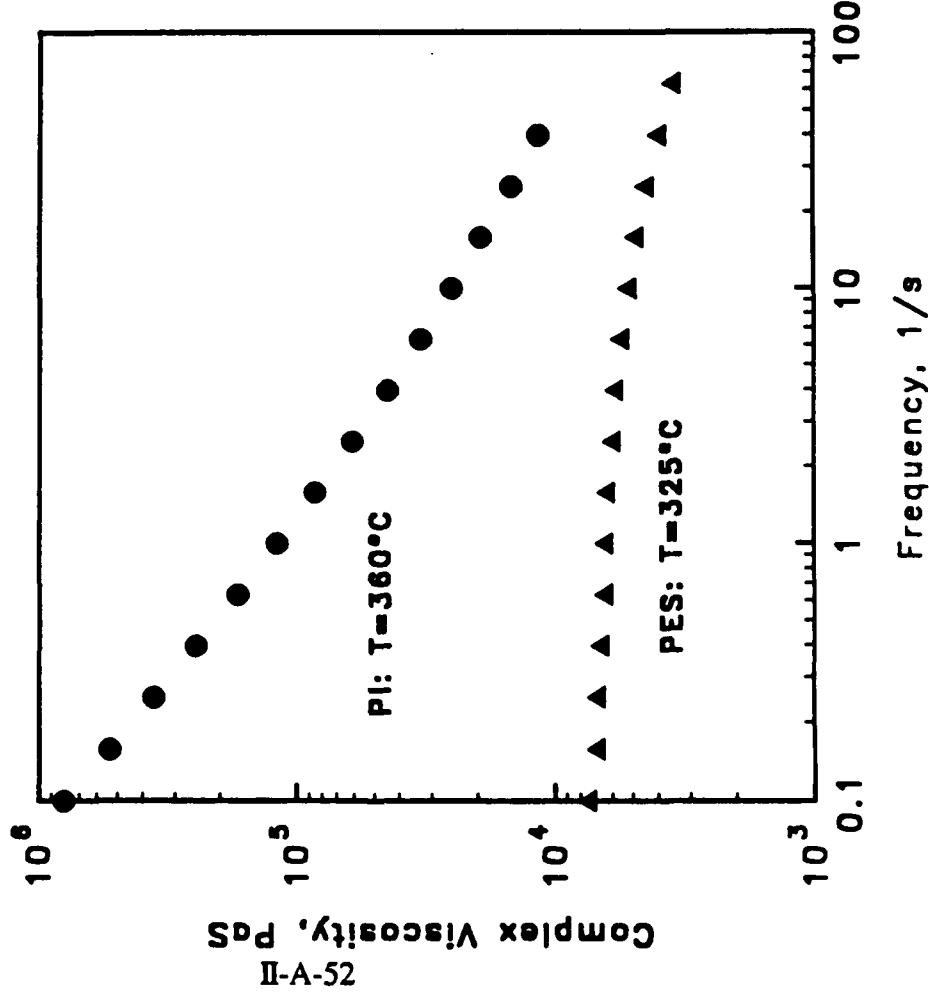
- Processing temperature
- Viscosity
- Composition

TORQUE RHEOMETER PROCESSING CONDITIONS

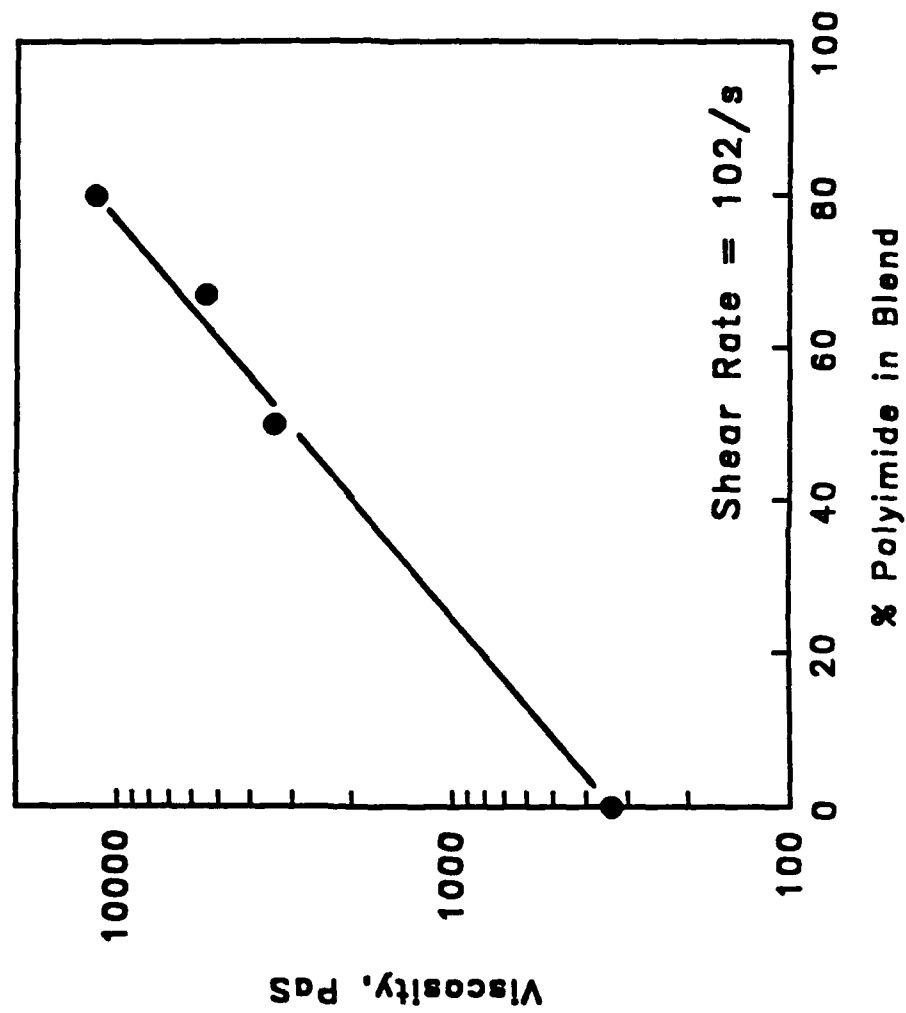


II-A-51

POLYIMIDE AND POLYETHERSULFONE MELT RHEOLOGY

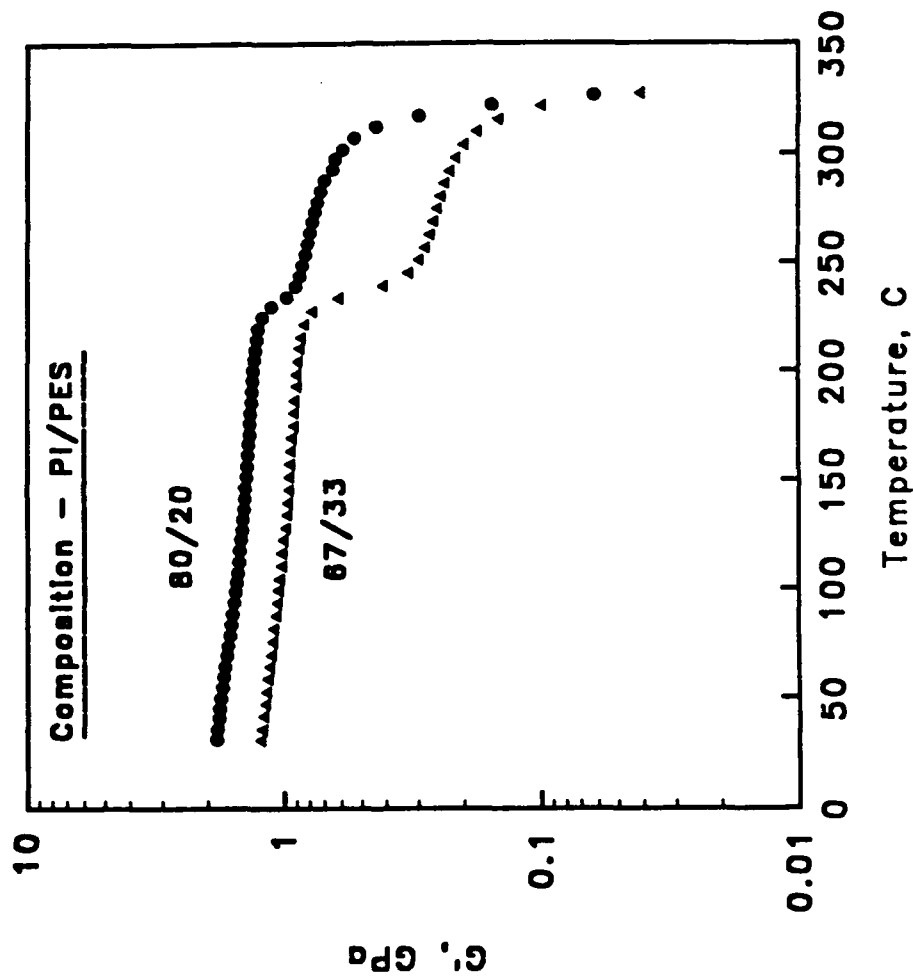


POLYIMIDE/PES BLEND VISCOSITY



II-A-53

POLYIMIDE/PES MELT BLEND TORSIONAL MODULUS



II-A-54

SUMMARY

- Melt blending polyimide with PES can result in a homogeneous, translucent blend similar to those obtained by coprecipitation from a mutual solvent
- The only homogeneous translucent blends obtained required the major phase to be the polyimide. Under these conditions, the PES acts as a flow aid for the polyimide, which cannot be melt processed by itself
- DSC and dynamic mechanical analysis does not show molecular miscibility of the melt blends, even those which are translucent
- The 67/33 PI/PES blend, while having a relatively high viscosity, was melt processable into rods and pellets. Both the 67/33 and 80/20 blends could be compression molded into films and sheets

FUTURE WORK

- Continue scale up of ultrahigh performance polyimide melt blend processing
- Extend processing technology to other blend systems

OTHER CRITERIA, 1990/1991

With complete or partial URI support:

Some 8 Ph.D.'s awarded

About 45 publications appeared or are in press

5 Patents issued or applied for

SUMMARY OF IONOMER RESEARCH UNDER URI SPONSORSHIP

- **Synthesis and Characterization of Novel Ionomers**

**Sulfonated Polyethersulfone (SPES)
Sulfonated Poly(ether ether ketone)
(SPEEK)
Carboxylated Poly(2,6 dimethyl-1,4
phenylene oxide) (CPPO)
Sulfonated Poly(2,6 dimethyl-1,4
phenylene oxide) (SPPO)**

- **Ionomer Blends**

**SPES with Different Sulfonation Levels
CPPO with Polystyrene (CPPO/PS)
Sulfonated Polystyrene with Poly(ethyl
acrylate co-vinyl pyridine) SPA/EAVP**

- **Results**

**The maximum tolerable difference in
sulfonation level for miscibility in
SPES blends is 10%
CPPO/PS blends exhibit unusual phase
behavior, including the occurrence of
critical double points
SPS/EAVP blends are compatibilized by
acid-base or complexation interactions**

- **Development of the "Ionic Network" model to
explain compatibilization by ionic interactions.**

UNIVERSITY OF PENNSYLVANIA

Professor Alan G. McDiarmid

WASHINGTON D.C., JANUARY 14, 1992

U.R.I. PROGRAM
UNIVERSITY OF PENNSYLVANIA

"POLYMERS BY NON-REDOX PROCESSES:
SYNTHESIS, PHYSICAL STUDIES
AND APPLICATION"

CONTRACT NO.: N00014-86-K-0766
SEPTEMBER 16, 1986 – OCTOBER 31, 1989

GRANT NO.: N00014-90-J-1559
NOVEMBER 1, 1989 – DECEMBER 31, 1991

[NO-COST EXTENSION TO JUNE 30, 1992]

PRINCIPAL INVESTIGATORS:

A.G. MACDIARMID
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA, PA
AND

A.J. EPSTEIN
DEPARTMENT OF PHYSICS &
DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY, COLUMBUS, OH

OUTLINE

POLYMERS BY NON-REDOX PROCESSES

- **Participants**
- **Objectives**
- **Rationale**
- **Polyaniline: Synthetic Metal for Technology**
- **The Polyanilines — Selected Examples of Achievements**
 - **Chemistry and Processing**
 - **Physical Properties, Structure and Electronic Concepts**
 - **Aerospace Applications**
- **Reports of Subcontractors**
- **Request for Further Funding for Microwave Processing/
Welding/Repair of Plastics Using Conducting Polymers**
- **Appendices**
 - **Pre- and Post-Doctoral Fellows**
 - **Industrial/Academic Interactions**
 - **Invited Presentations**
 - **Publications and Patents**
 - **Fiscal Budget**

PARTICIPANTS

POLYMERS BY NON-REDOX PROCESSES: SYNTHESIS; PHYSICAL STUDIES AND APPLICATION

	<u>% of Research Funds</u>
1. University of Pennsylvania	≈ 40
(a) Department of Chemistry (A.G. MacDiarmid) (Synthesis, processing, doping)	
(b) Department of Materials Science and Engineering (G.C. Farrington) (Electrochemistry studies)	≈ 18
2. The Ohio State University	≈ 26
Department of Physics (A.J. Epstein) (Physics studies)	
3. Lockheed Missiles & Space Corporation	≈ 10
Polymer Chemistry Research Group (J. Zegarski) (Technologically oriented R&D)	
4. University of Rhode Island	≈ 2
Department of Chemistry (S.C. Yang) (Spectroelectrochemical studies)	
5. Montclair State College	≈ 2
Department of Chemistry (B.D. Humphrey) (Polymer composites)	
6. Drexel University	≈ 2
Department of Chemistry (Y. Wei) (Thermal properties of polymers)	
7. Rensselaer Polytechnic Institute	*
Department of Chemistry (G.E. Wnek) (Polymer Characterization)	

* Due to lack of funds Dr. Wnek's group could not perform research from 4/1/90-5/31/90, as well as during their no-cost extension period of 6/1/90-12/31/90.

POLYMER LIQUID CRYSTALS

1. Kent State University	≈ 58
Liquid Crystal Institute (J.W. Doane)	
2. Case Western Reserve University	≈ 17
Department of Macromolecular Science (V. Percec)	
3. University of North Carolina	≈ 25
Department of Chemistry (E.T. Samulski)	

OBJECTIVES

- OBTAIN A FUNDAMENTAL UNDERSTANDING OF THE SYNTHESIS, PROCESSING, DOPING AND ELECTRONIC/MAGNETIC/OPTICAL PHENOMENA IN CONDUCTING POLYMERS —
- DETERMINE FACTORS CONTROLLING ULTIMATE UPPER LIMIT OF CONDUCTIVITY —
- — LEADING TO THE DESIGN OF CONDUCTING POLYMERS EXHIBITING PRESELECTED DESIRABLE ELECTRONIC, OPTICAL, MAGNETIC, THERMAL, CHEMICAL, MECHANICAL, ETC., PROPERTIES
- TRAIN UNDERGRADUATE AND GRADUATE STUDENTS AND POST-DOCTORAL FELLOWS IN THIS HIGHLY INTERDISCIPLINARY AREA OF POLYMER SCIENCE
- HIRE NEW FACULTY IN CHEMISTRY AND MATERIALS SCIENCE SO AS TO LEAVE A LEGACY FOR THE FUTURE IN POLYMER MATERIALS SCIENCE AFTER EXPIRATION OF CONTRACT

RATIONALE

MATERIALS SCIENCE IS A MATERIALS LIMITED FIELD

- QUANTUM JUMPS OCCUR WHEN MATERIALS WITH NOVEL UNEXPECTED PROPERTIES ARE SYNTHESIZED.

THEREFORE, EMPHASIS ON:

- SYNTHESIS OF NEW CONDUCTING POLYMERS
- PROCESSIBILITY (CRITICAL TO THE TECHNOLOGICAL USE OF A POLYMER)
- PHYSICS STUDIES TO DEVELOP FUNDAMENTAL UNDERSTANDING OF ELECTRONIC, OPTICAL AND MAGNETIC PROPERTIES LEADING TO —

DESIGN OF NEW DERIVATIVE OF POLYANILINE EXHIBITING CONTROLLED PROPERTIES

- | | |
|--------------|-------------------|
| • CHEMICAL | • ELECTROCHEMICAL |
| • PHYSICAL | • OPTICAL |
| • MAGNETIC | • ELECTROOPTIC |
| • ELECTRICAL | • NONLINEAR OPTIC |
| • ELECTRONIC | • DIELECTRIC |
| • MECHANICAL | • ELECTROCHROMIC |

1930's —————→

- CONVENTIONAL ORGANIC POLYMERS HAVE PLAYED AN INCREASINGLY HIGHLY IMPORTANT ROLE IN TECHNOLOGY BECAUSE OF THEIR CHARACTERISTIC MECHANICAL, OPTICAL, ELECTRICALLY-INSULATING AND CHEMICAL PROPERTIES —
 - AS SUBSTITUTES FOR SELECTED METALS, WOOD, CERAMICS AND NATURALLY-OCCURRING POLYMERS AND AS NEW MATERIALS IN THEIR OWN RIGHT
-

LATE 1970's —————→

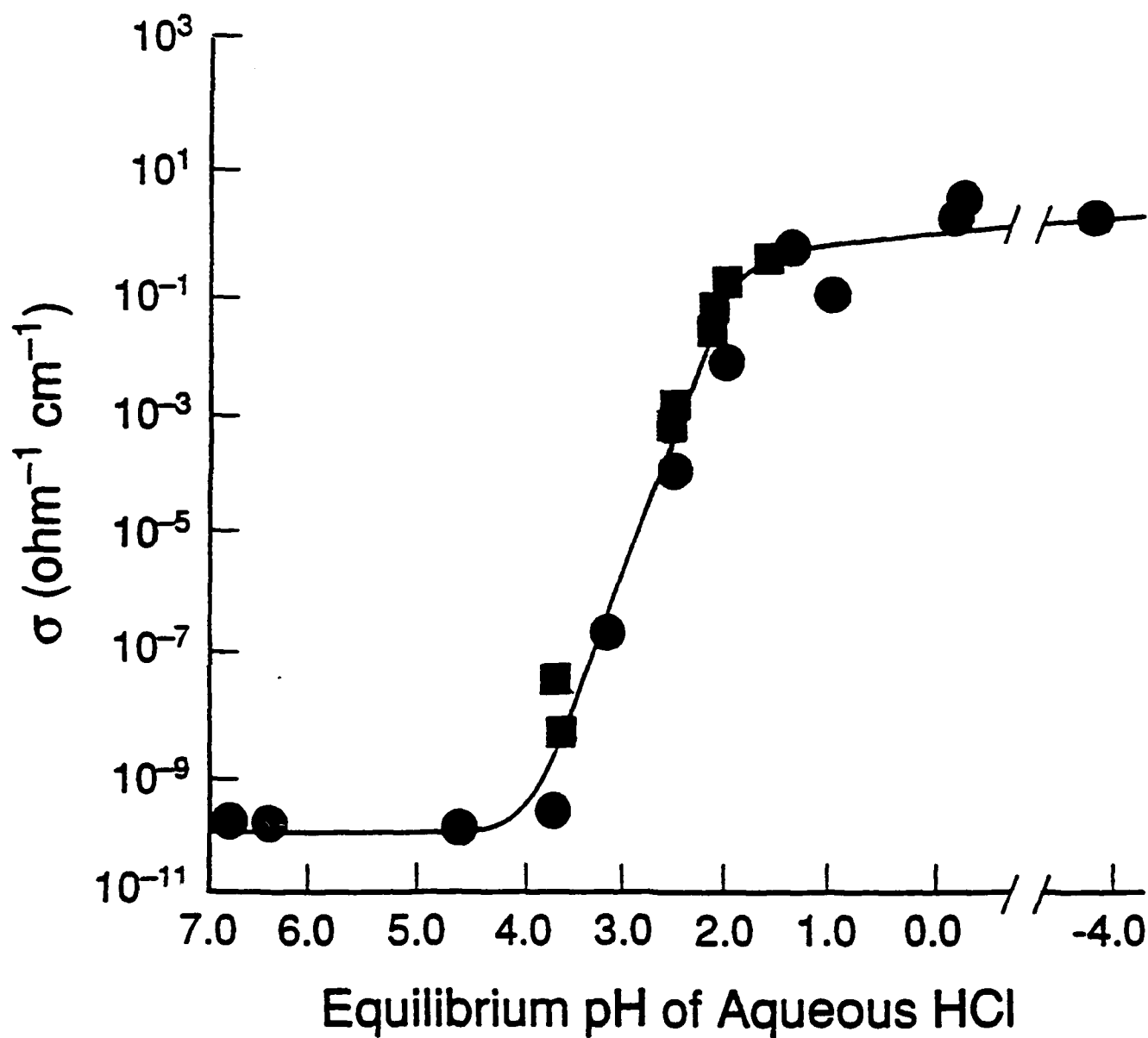
- EMERGENCE OF A NEW ERA IN ORGANIC POLYMERS
- p- AND n-DOPING OF AN ORGANIC POLYMER TO THE METALLIC STATE
- ORGANIC POLYMERS HAVING THE ELECTRONIC AND MAGNETIC PROPERTIES OF A METAL BUT RETAINING THE MECHANICAL, ETC. PROPERTIES OF CONVENTIONAL POLYMERS

**POLYANILINE:
SYNTHETIC METAL
FOR TECHNOLOGY**

1986 – Present

**Evolution
From Academia
To Commercial Production
– and Beyond ?**

PROTONIC ACID DOPING
OF POLYANILINE



CHIANG and MacDIARMID (NSF - 1986)

II-B-10

POLYANILINE

PAPERS AND PATENTS *

1986 108

1987 221

1988 236

1989 383

1990 309

1991 281

Total 1538

* *CHEMICAL ABSTRACTS* (to *DECEMBER 17, 1991*) .

>120 Publications* and Patents
(Issued and/or Filed)
on Chemistry, Electrochemistry, Physics,
Structure, and Bonding of Polyanilines by
Epstein and MacDiarmid
January 1, 1986 – December 31, 1991

*** Published or Accepted for Publication**
(most funded in whole or in part
from URI Contract/Grant)

POLYANILINE

TECHNOLOGICAL ACTIVITY

- **MAY 6, 1991 :**

ANNOUNCEMENT OF A JOINT VENTURE BY ALLIED-SIGNAL CORP. (USA), AMERICHEM CORP. (USA) AND ZIPPERLING KESSLER & CO. (GERMANY) TO MANUFACTURE LARGE QUANTITIES OF POLYANILINE AND ITS BLENDS WITH PVC, NYLONS, ETC., FOR USE IN EMI SHIELDING, ETC. THESE MATERIALS ARE NOW BEING SOLD.

- **APRIL 22, 1991 :**

ANNOUNCEMENT OF JOINT VENTURE BY UNIAX CORP. (USA) AND NESTE OY (FINLAND) FOR RESEARCH AND DEVELOPMENT OF POLYTHIOPHENES AND POLYANILINE.

- **APRIL 10, 1991 :**

ANNOUNCEMENT BY NESTE OY (FINLAND) OF START-UP OF PILOT PLANT PRODUCTION OF POLYANILINE AND POLYTHIOPHENE DERIVATIVES TO SUPPORT APPLICATION DEVELOPMENT OF CONDUCTING POLYMERS.

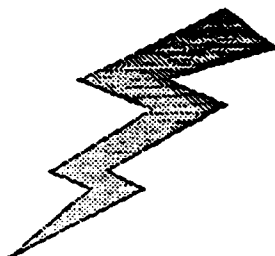
- **FEBRUARY 28, 1990 :**

ANNOUNCEMENT BY LOCKHEED CORP. (USA) AND HEXCEL CORP. (USA) OF A JOINT VENTURE TO MANUFACTURE POLYANILINE AND ITS BLENDS.

- **1987 :**

MANUFACTURING AND SALES BY BRIDGESTONE CORP. (JAPAN) AND SIEKO CORP. (JAPAN) OF RECHARGEABLE POLYANILINE BATTERIES.

VERSICON™



Inherently Conductive Polymer

Produced By

Allied-Signal Inc.

Potential Commercial Applications:

Electromagnetic Shielding

Cable Shielding

Electrostatic Control

Conductive Coatings

Resistive Heating

Sensors



VERSICON™ CONDUCTIVE POLYMER

Appearance:	Dark Green Powder
Conductivity (Compacted Powder):	2-4 Siemen/cm
Resistivity (Compacted Powder):	0.50-0.25 ohm-cm
Moisture Content:	3-4 wt %
Particle Size Range:	3-100 Microns
Specific Gravity:	1.36
Bulk Density:	18.8 lb/cu ft
Surface Area (BET):	5-20 m ² /g
Temperature Limits,	
Long Term (Years) Service:	100°C
Short Term (Minutes) Processing:	240°C
Solubility:	Insoluble in common solvents such as water, alcohols, ethers, hydrocarbons.
Chemical Nature:	Acidic, incompatible with most bases

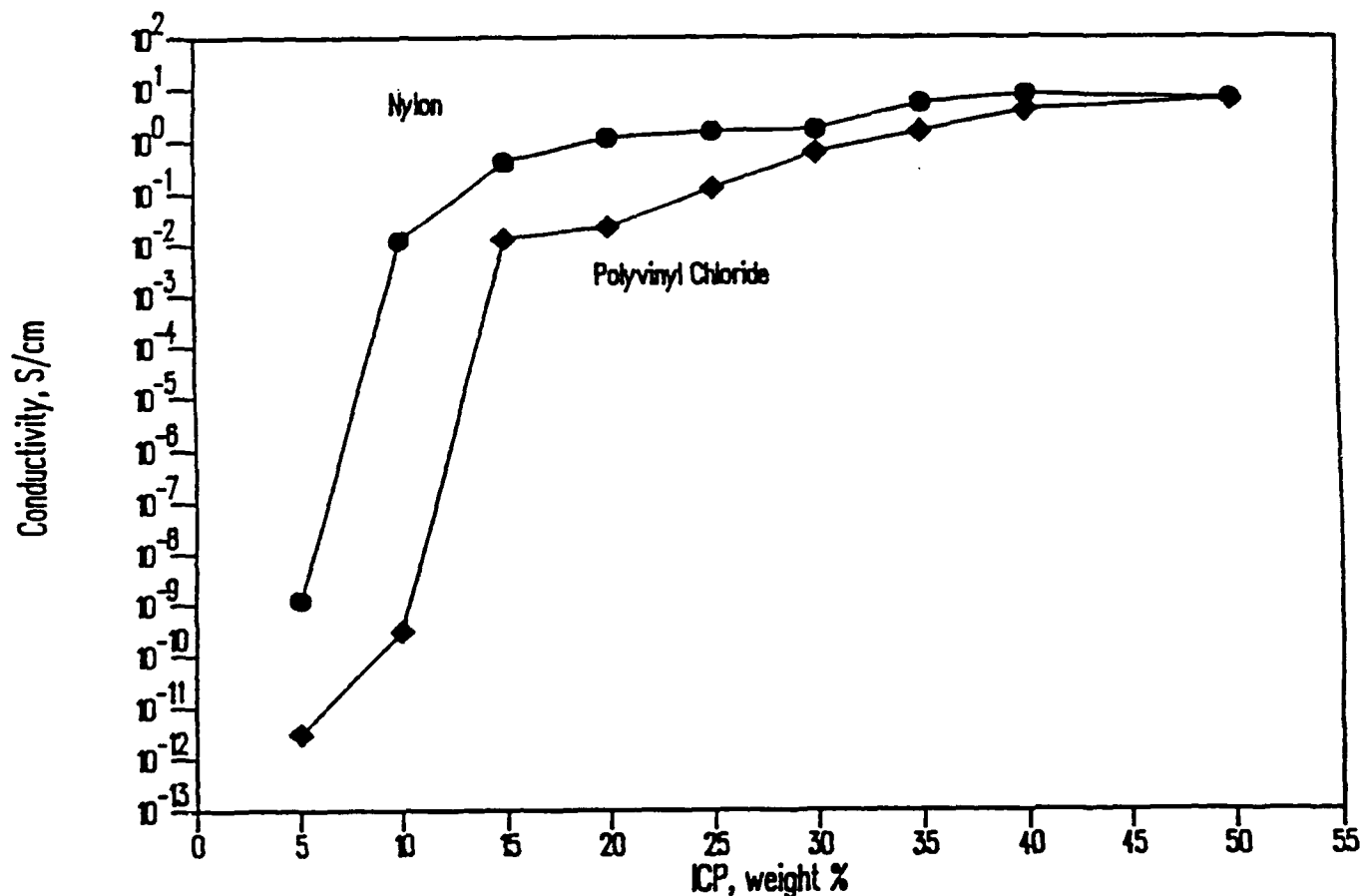
VERSICON is an inherently conductive polymer produced by Allied-Signal Inc., patents pending.

For additional information or samples contact:

D.G. Frick
ALLIED-SIGNAL INC.
20 Peabody Street
Buffalo, NY 14210
Telephone (716) 827-6357
FAX (716) 827-6221

All statements, and data given herein are believed to be accurate and reliable but are presented without guaranty, warranty, or responsibility of any kind, express or implied. Statements or suggestions concerning possible use of our products are made without representation or warranty that any such use is free of patent infringement, and we are not recommending to infringe any patent. The user should not assume that all safety measures are indicated, or that other measures may not be required.

Percolation Curves for ICP in Nylon and Polyvinylchloride



**THE DOPED POLYANILINE BECOMES PARTLY CRYSTALLINE
(X-RAY) DURING THE PROCESSING OF THE POLYMER
(INVOLVING SHEARING) TO FORM BLENDS WITH VARIOUS
THERMOPLASTIC AND NON-THERMOPLASTIC PLASTICS.**

L.W. Shacklette, N.F. Colaneri, V.G. Kulkarni and B. Wessling,
in 49th ANTEC Conference Proceedings,
Society of Plastic Engineers and Plastic Engineering,
Montreal, Canada, (May 5-9), p. 664 (1991).

The commercial availability of large quantities of doped polyaniline now facilitates ready evaluation of its potential large-scale technological applications.

**For example*: Microwave welding,
Processing and
Repair of conventional
polymers**

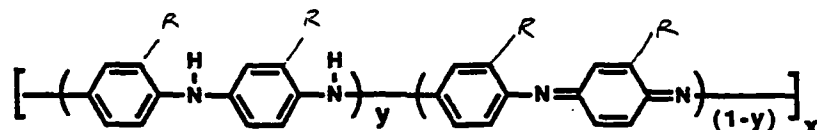
*** [See later sections by Epstein (OSU) & Zegarski (Lockheed)]**

**Selected examples of
advances in the
chemistry and processing
of polyanilines
since the last URI review**

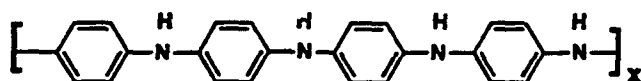
(Washington D.C., June 21-22, 1990)

"THE POLYANILINES" *

- A CLASS OF CONDUCTIVE POLYMERS DERIVED FROM THE BASE FORM OF GENERAL COMPOSITION :

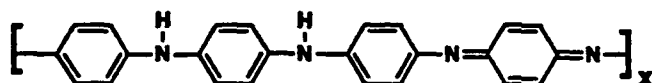


THE AVERAGE OXIDATION STATE IS GIVEN BY THE VALUE OF $(1 - Y)$



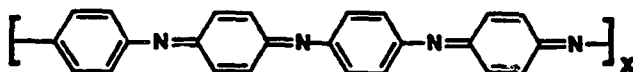
COMPLETELY REDUCED

LEUCOEMERALDINE
BASE
 $(1 - y) = 0$



HALF OXIDIZED

EMERALDINE
BASE
 $(1 - y) = 0.5$



COMPLETELY OXIDIZED

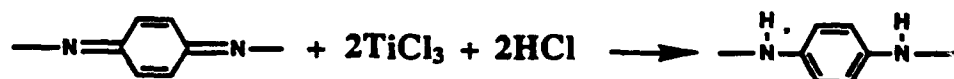
PERNIGRANILINE
BASE
 $(1 - y) = 1$

- SOME OR ALL OF THE $-\text{N} =$ GROUPS CAN BE PROTONATED BY AQUEOUS ACIDS TO YIELD A RANGE OF CORRESPONDING SALTS, SOME OF WHICH ARE HIGHLY CONDUCTING.

* "MIXED" OXIDATION STATE POLYMER

ANALYSIS : (1) ELEMENTAL : C, H, N

(2) OXIDATION STATE



SYNTHESIS OF
EMERALDINE OXIDATION STATE
OF
POLYANILINE

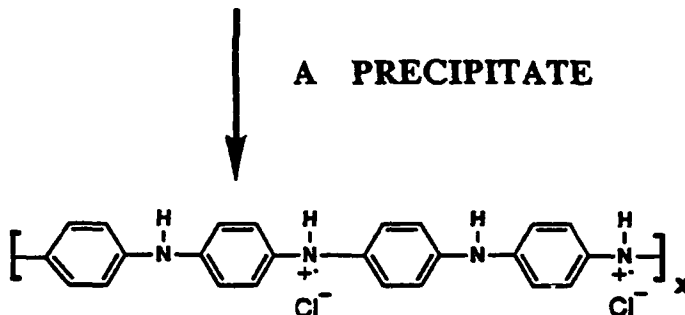
SYNTHESIS

CHEMICAL OR ELECTROCHEMICAL OXIDATIVE POLYMERIZATION OF ANILINE IN AQUEOUS ACID

CHEMICAL



A PRECIPITATE



EMERALDINE.HCl

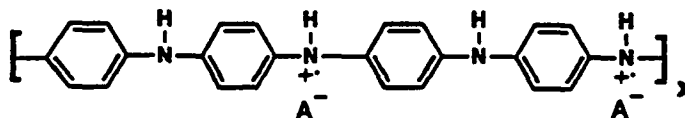
ELECTROCHEMICAL



Anode ~ 0.7V
(vs. SCE)

$\text{A}^- = \text{Cl}^-, \text{HSO}_4^-,$
 $\text{ClO}_4^-, \text{BF}_4^-, \text{etc.}$

FILMS OF



EMERALDINE SALT

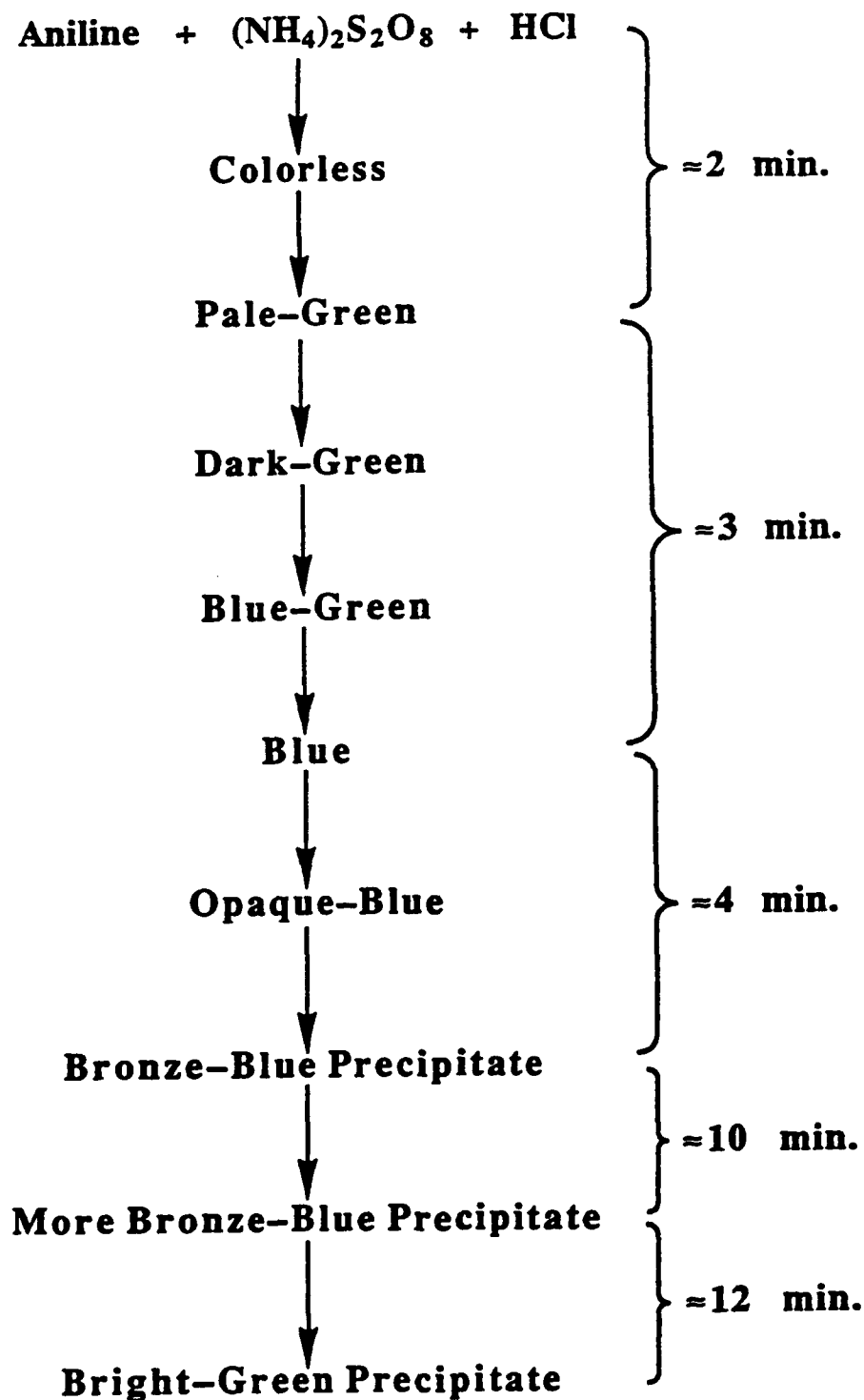
POLYANILINE SYNTHESIS BY THE CONVENTIONAL METHOD *

**POLYANILINE IN THE EMERALDINE OXIDATION STATE
IS NOT THE FIRST FORMED POLYANILINE.**

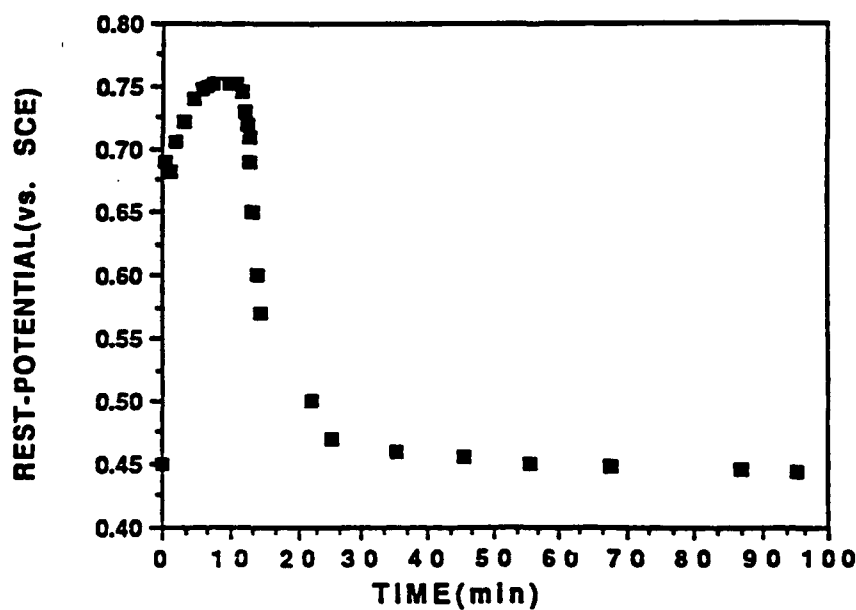
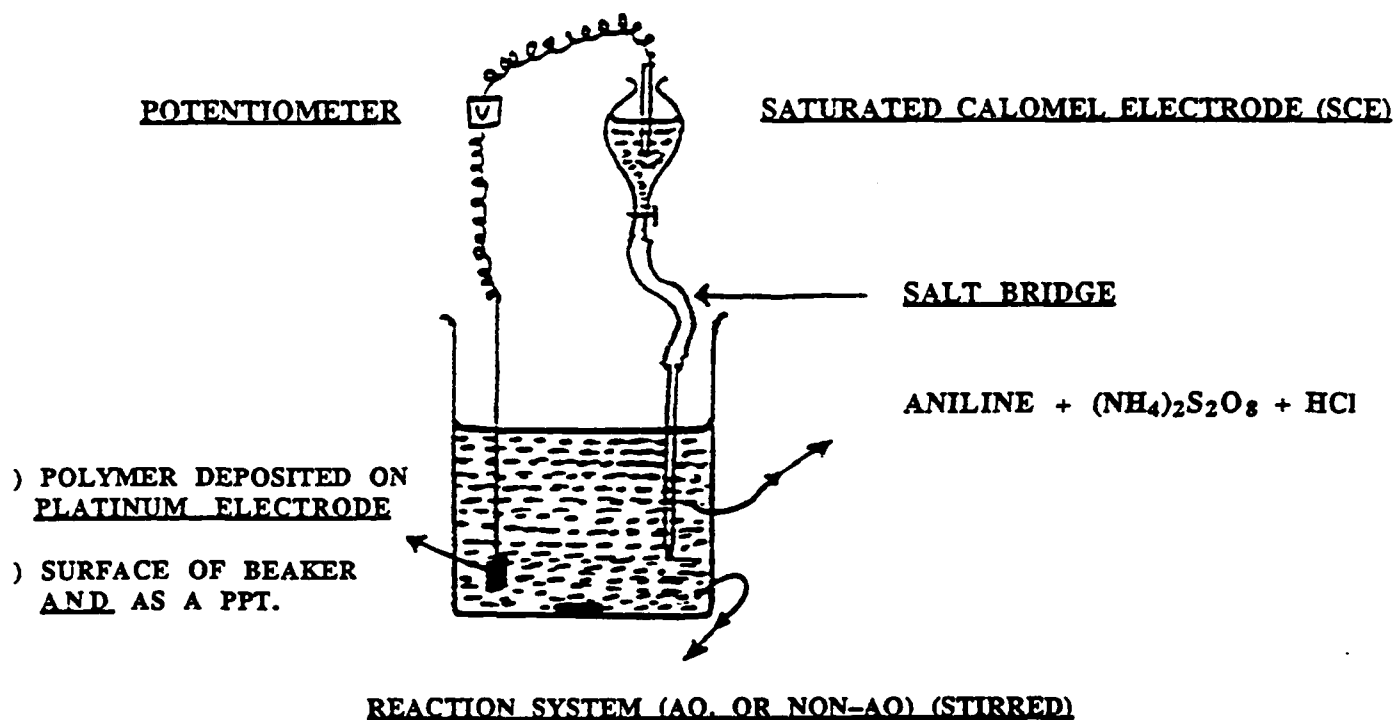
THE PERNIGRANILINE OXIDATION STATE IS FORMED FIRST !

* A.G. Green and A.E. Woodhead, J. Chem. Soc. Trans., 97, 2388 (1910); and
J. Chem. Soc. Trans., 101, 1117 (1912).

COLOR CHANGES DURING POLYMERIZATION



REST-POTENTIAL PROFILING TECHNIQUE FOR STUDYING CONDUCTING POLYMERS

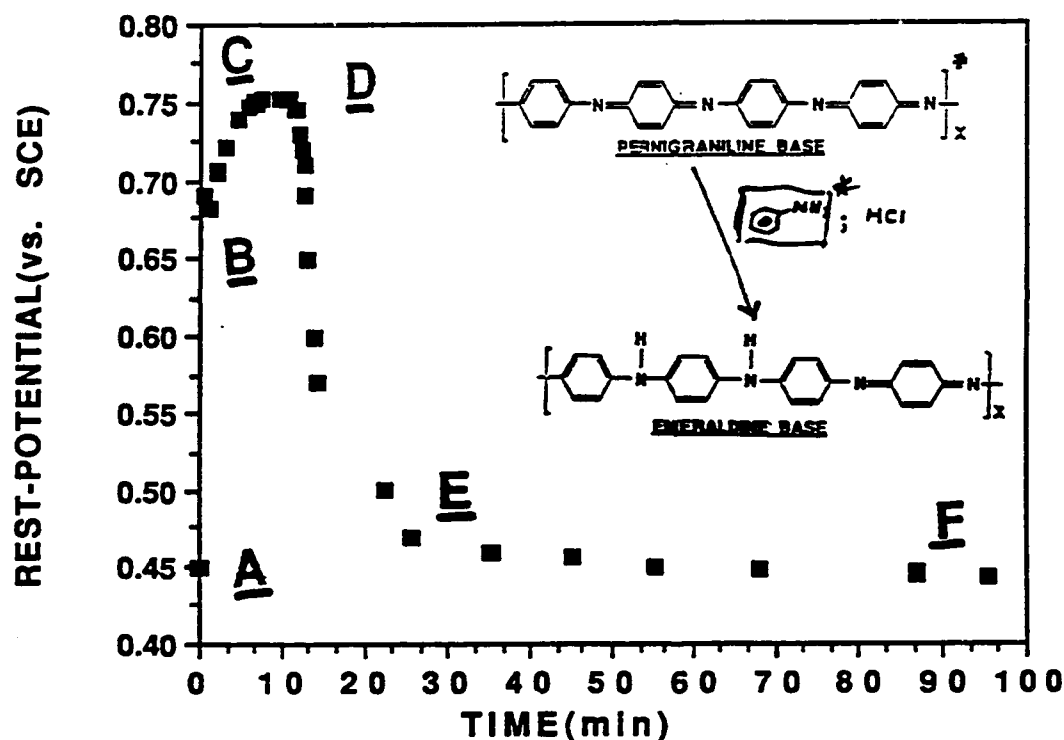


(=0°C)
II-B-24

REST-POTENTIAL PROFILING OF ANILINE POLYMERIZATION WITH ACIDIC AMMONIUM PEROXYDISULFATE

ANILINE: $(\text{NH}_4)_2\text{S}_2\text{O}_8 \approx 4:1$

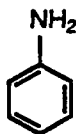
ALL $(\text{NH}_4)_2\text{S}_2\text{O}_8$ CONSUMED
(SHOWN IN A SEPARATE STUDY)



($\approx 0^\circ\text{C}$)

- ISOLATED AS THE BASE FORM AFTER TREATMENT WITH aq. 0.1N NaOH (FOR PERNIGRANILINE; 0.1N NH_4OH FOR EMERALDINE)
- PROVED IN A SEPARATE STUDY
- OXIDATION PROCEEDS RAPIDLY AFTER INITIAL OXIDATION STEP.

ISOLATION OF POLYANILINE IN THE PERNIGRANILINE OXIDATION STATE DURING THE CONVENTIONAL SYNTHESIS OF POLYANILINE



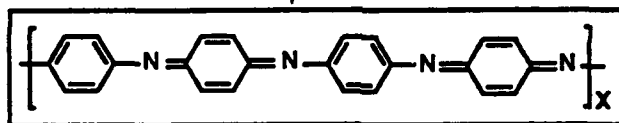
ANILINE (~20 mL in ~300 mL aq. 1.0 N HCl)

- (i) $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (11.5 g); aq. 1.0 N HCl (200 mL); -6°C ; stir.

(ii) Monitor Potential Increase to -0.75 V (SCE).

(iii) Pour into aq. 0.1 N NaOH (10 litres) at -0°C ; adjust pH ≈ 9 ; stir for ≈ 60 s; filter; wash with water (5 liters) and then with CH_3CN .

(iv) Dry under dynamic vacuum for 72h/RT.



PERNIGRANILINE BASE

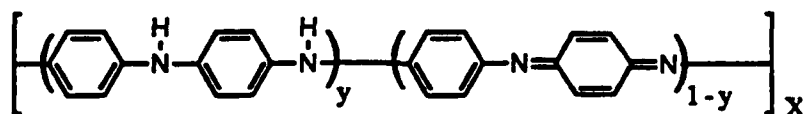
COLOR : BLACK

CONDUCTIVITY : $< 10^{-8}$ S/cm

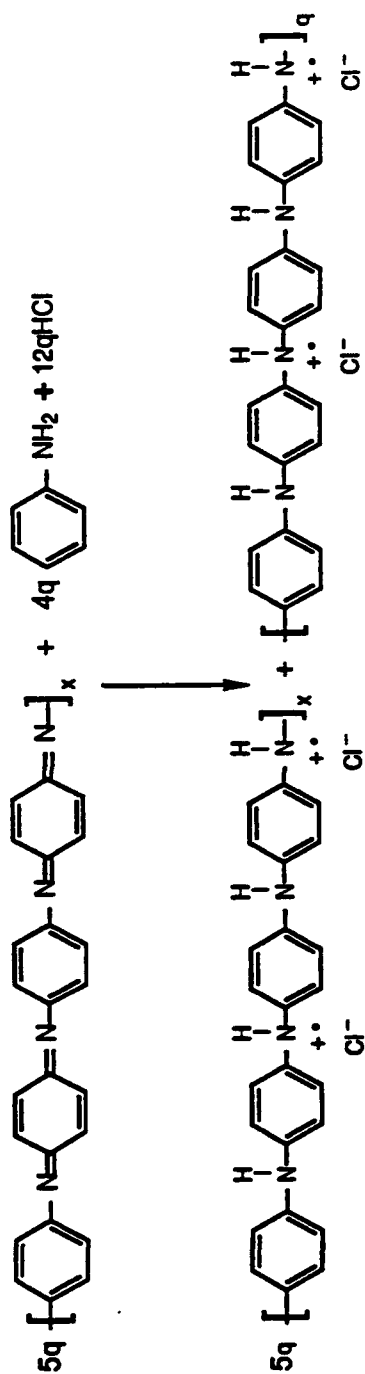
$V_{oc}(1.0 \text{ N HCl}) ; \text{RT} = -0.82 \text{ V (SCE)}$

ELEMENTAL COMPOSITION :

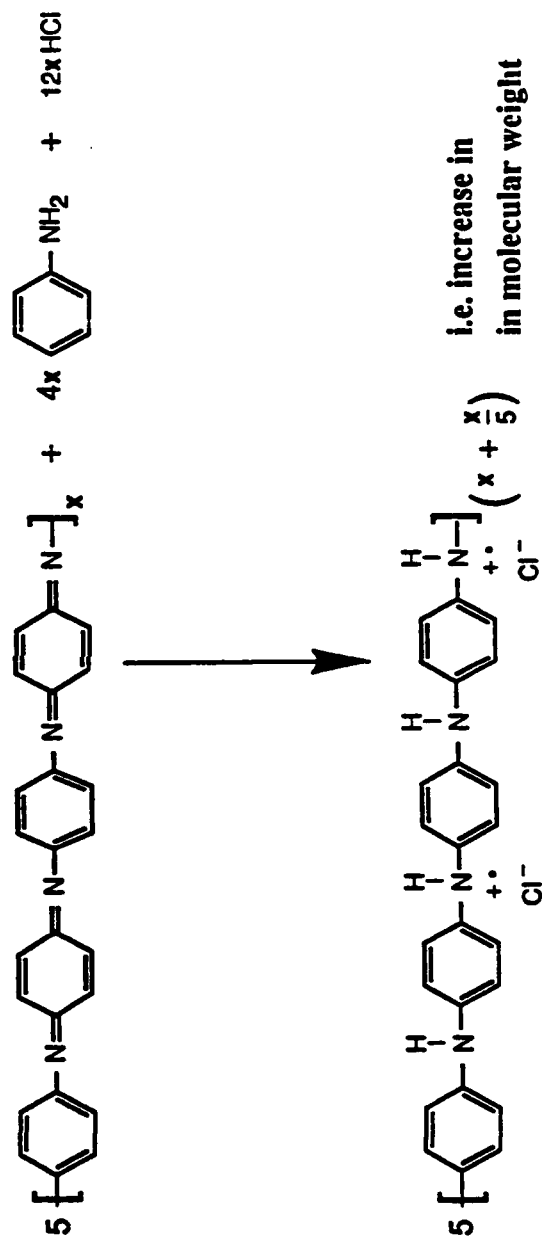
		<u>CARBON</u>	<u>HYDROGEN</u>	<u>NITROGEN</u>	<u>TOTAL</u>
<u>CALC. :</u>		80.00	4.44	15.56	100.00
<u>FOUND :</u>	(Prep 1)	79.35	4.31	15.41	99.07
	(Prep 2)	79.90	5.14	15.41	100.25
	(Prep 3)	78.97	5.00	15.58	99.55
	(Prep 4)	79.96	5.10	15.68	100.74



(1-y) = 0.96 ± 0.02 BY TiCl_3 TITRATION



OR



emeraldine oxidation state $\overline{M}_w = 64,452; \overline{M}_n = 25,283; \overline{M}_w/\overline{M}_n = 2.55$

$(NH_4)_2S_2O_8$

pernigraniline oxidation state
(isolated)

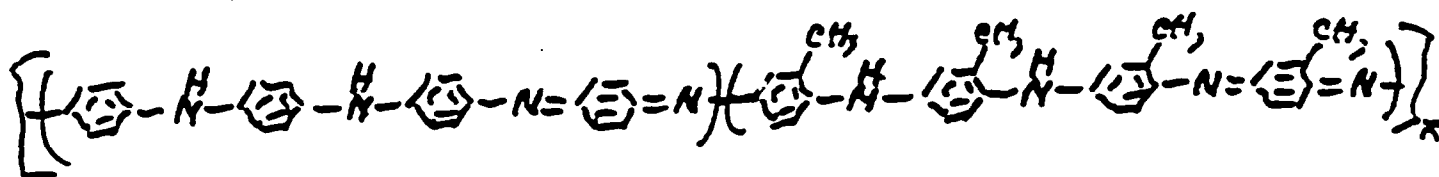
aniline



emeraldine oxidation state $\overline{M}_w = 89,633; \overline{M}_n = 68,089; \overline{M}_w/\overline{M}_n = 2.46$

(3 Cycles)

OR BLOCK CO-POLYMER



High Molecular Weight Polyaniline

aniline + $(\text{NH}_4)_2\text{S}_2\text{O}_8$ + H_2SO_4 + 5M LiCl

- $\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{H}_2\text{SO}_4$ less soluble than $\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{HCl}$ at -30°C
- Reduce the concentration of aniline species in solution
- This reduces the number of nucleation sites in solution
- This increases molecular weight

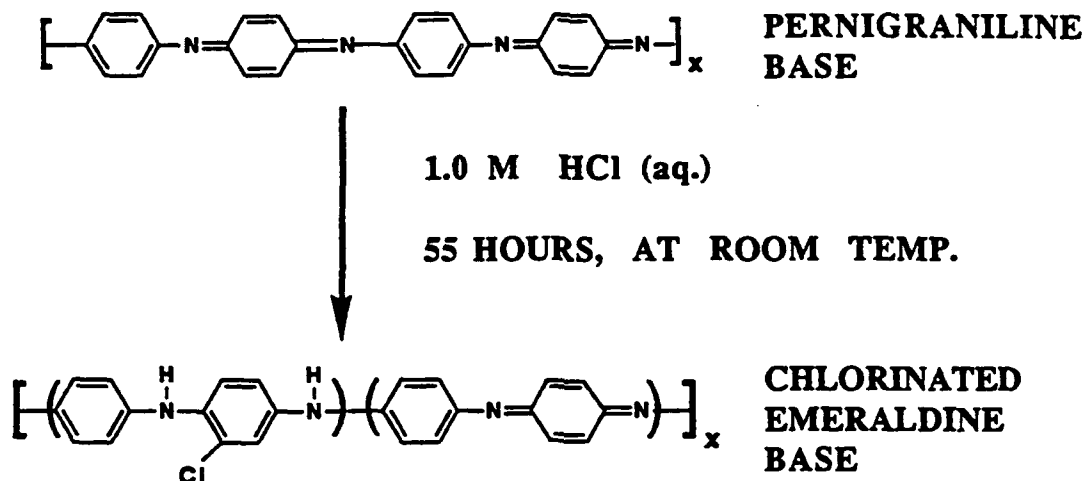
<u>METHOD</u>	<u>MOLECULAR WEIGHTS^a</u>		
	\bar{M}_w^b	\bar{M}_n	\bar{M}_w / \bar{M}_n
CONVENTIONAL SYNTHESIS	64,452	25,283	2.55
NEW SYNTHESIS	439,339 ^c	126,761	3.46

(a) G.P.C. (NMP solvent) vs. polystyrene standard

(b) Light scattering studies show that the true \bar{M}_w is $\sim 0.5(\text{G.P.C.})$

(c) i.e., true $\bar{M}_w \sim 220,000$

REACTION OF PERNIGRANILINE BASE WITH AQUEOUS HCl *



ELEMENTAL ANALYSIS :

	C%	H%	N%	Cl%	TOTAL %
CALC.	72.63	4.33	14.11	8.93	100.00
FOUND	73.41	4.63	13.57	8.60	100.21

- * EXPLAINS THE OBSERVATION THAT SOME SAMPLES OF POLYANILINE (EMERALDINE BASE) CONTAIN C-Cl BONDS BY ESCA [SALANECK, et. al.; HAGIWARA, et. al., 1988]

- * REACTION OF PERNIGRANILINE BASE WITH HCl IS MUCH SLOWER THAN ITS REACTION WITH ANILINE.
THEREFORE : EXCESS ANILINE SHOULD ALWAYS BE PRESENT

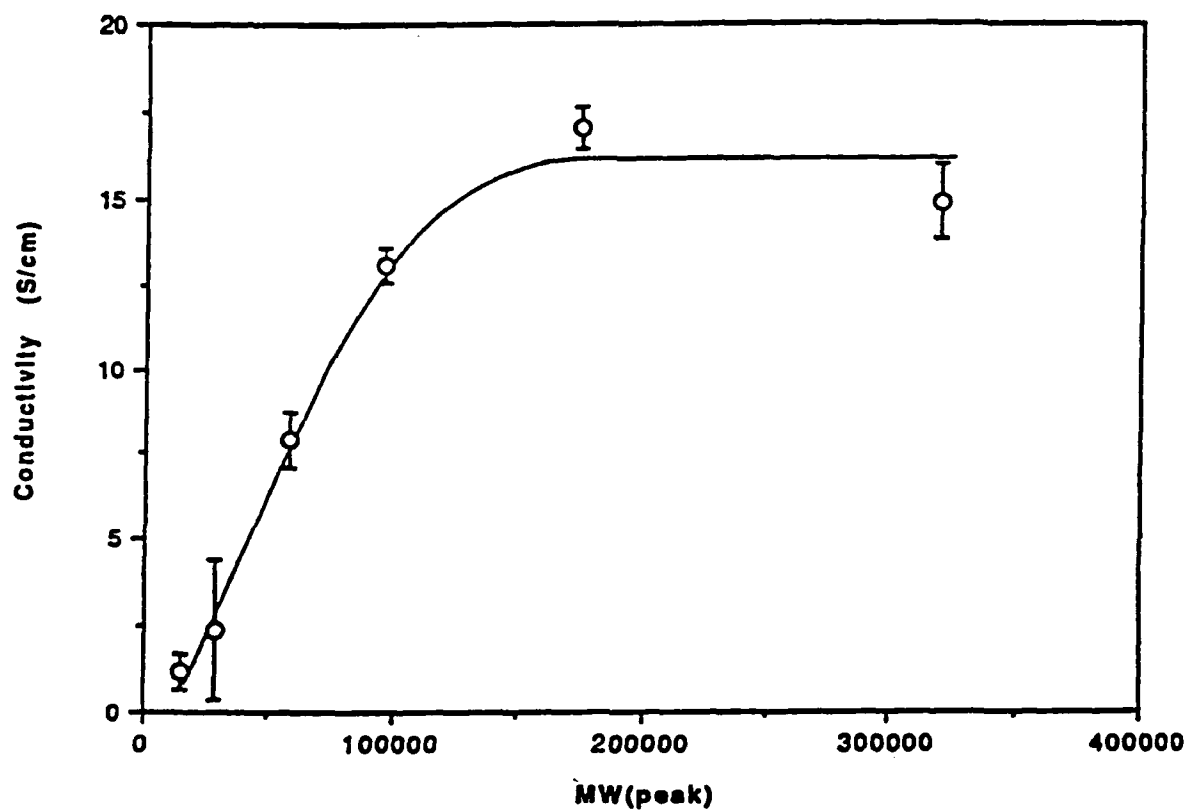
MOLECULAR WEIGHT* /
CONDUCTIVITY RELATIONSHIP

POLYANILINE
(EMERALDINE OXIDATION STATE)

* G.P.C. IN N.M.P. SOLUTION (POLYSTYRENE STANDARD)

CONDUCTIVITY vs. PEAK MOLECULAR WEIGHT

(4-PROBE; COMPRESSED PELLET)



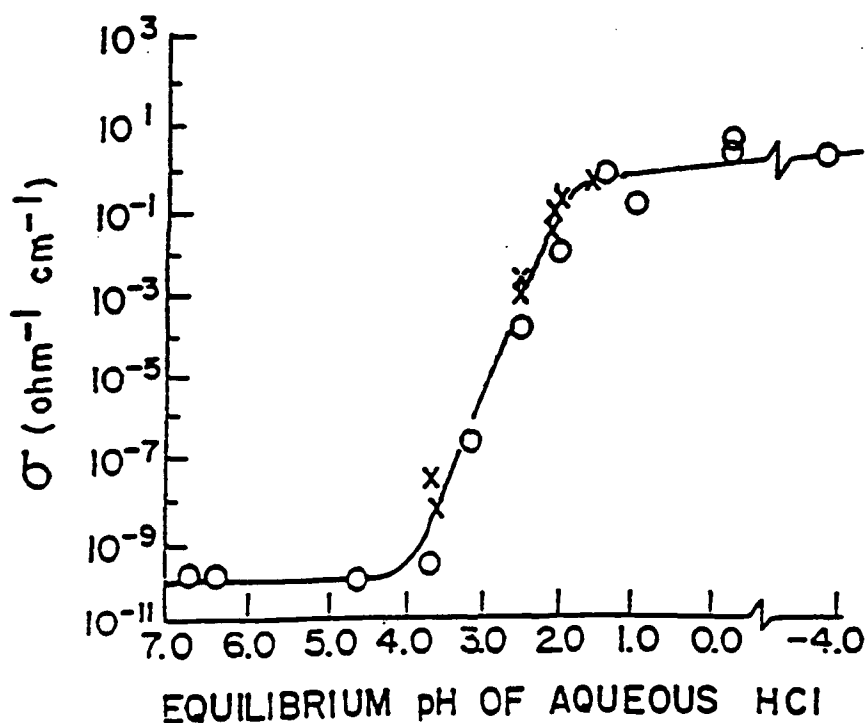
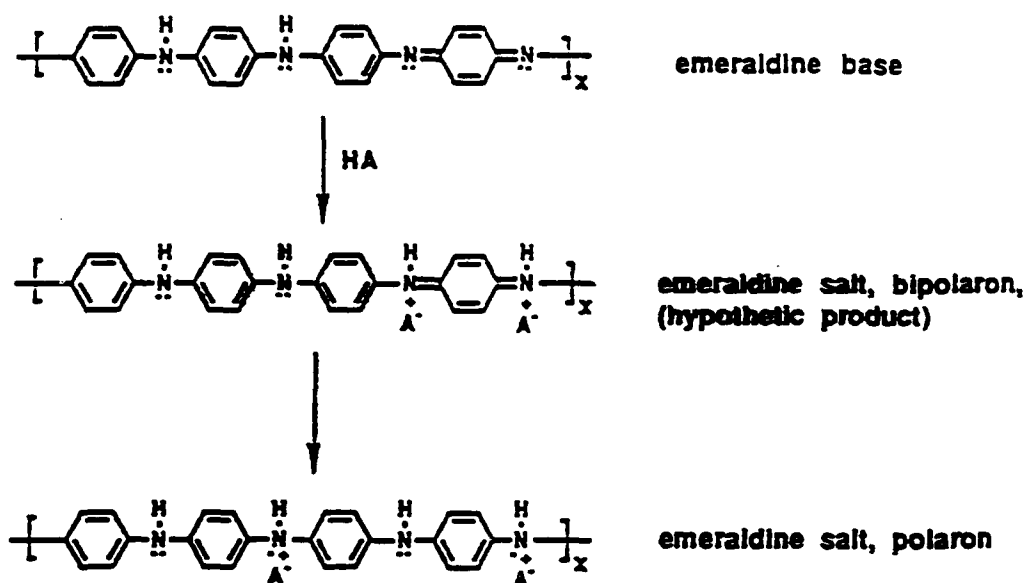
ALL SAMPLES ARE ESSENTIALLY AMORPHOUS
(VERY SMALL DEGREE OF CRYSTALLINITY)

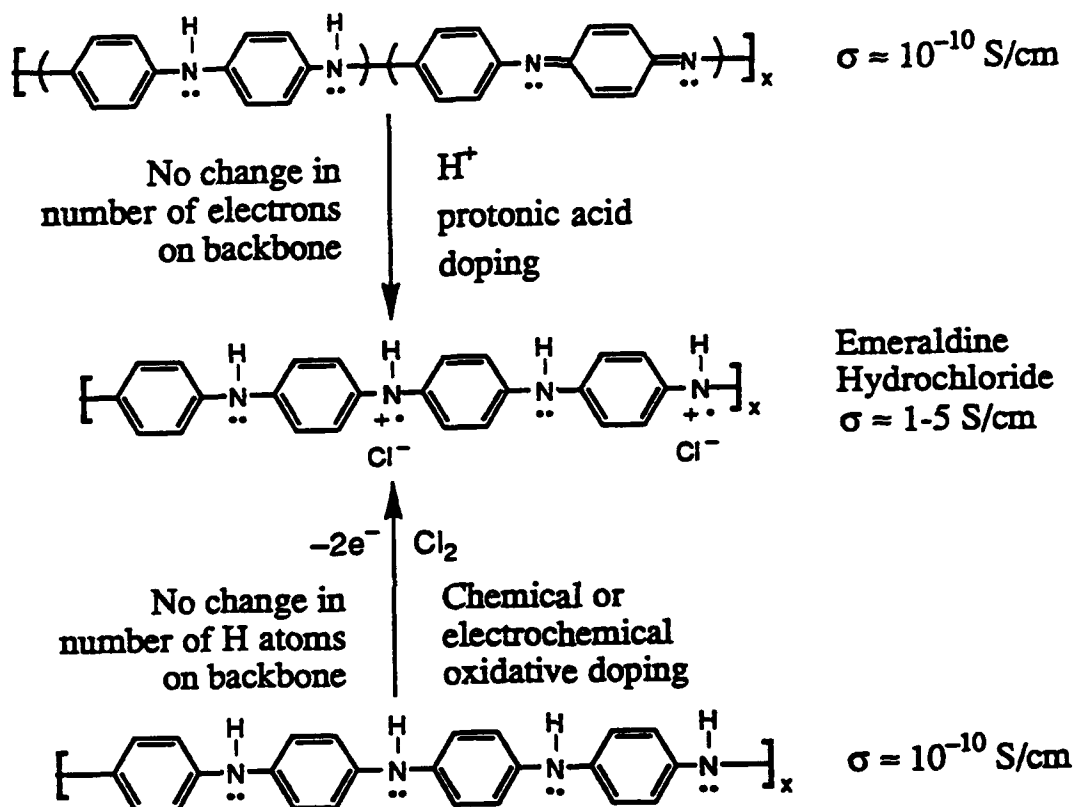
DOPING
OF
POLYANILINE

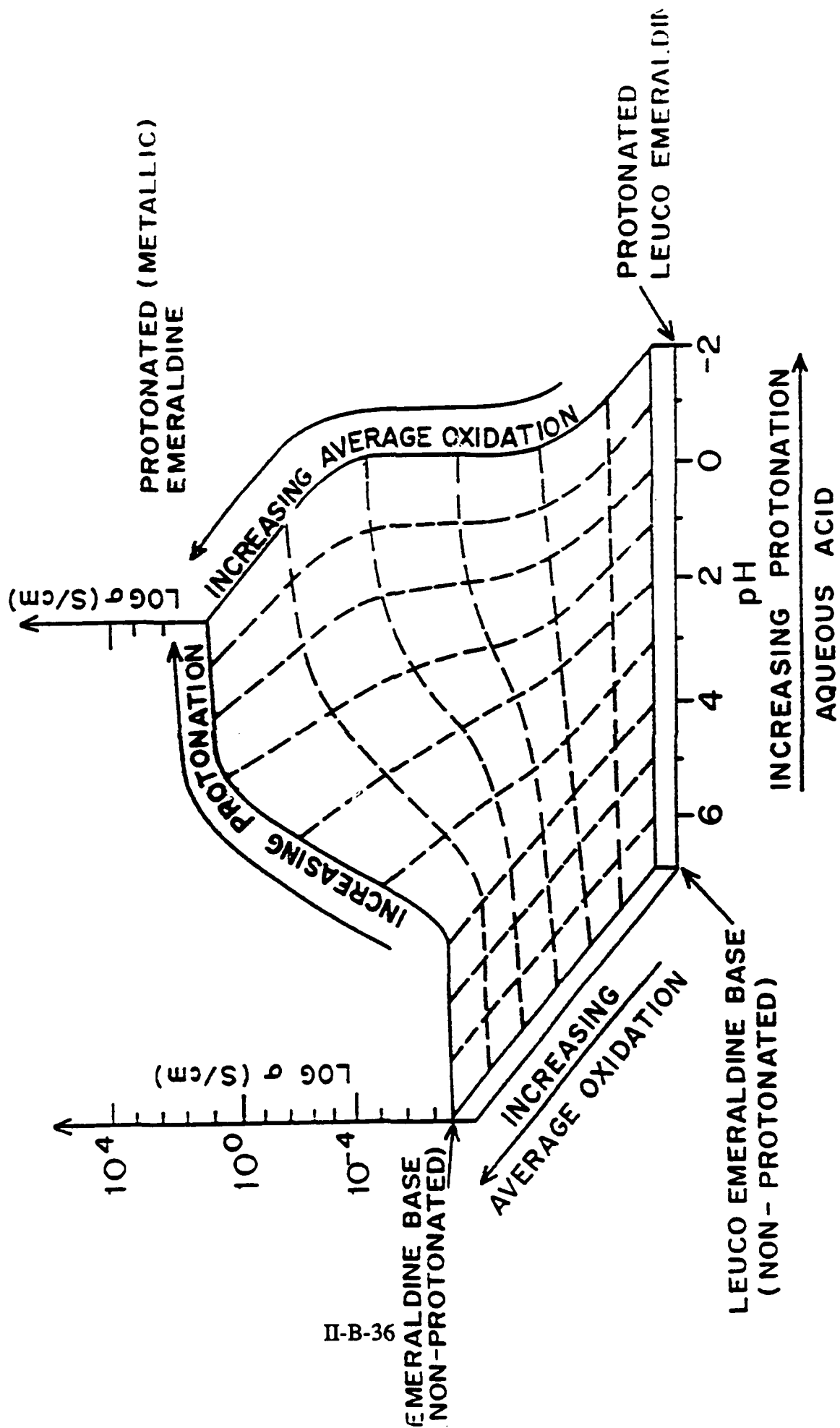
II-B-33

Protonic Acid Doping of Emeraldine Base

It is the half-oxidized form of polyaniline that can be protonically doped to yield an electrically conductive polymer.





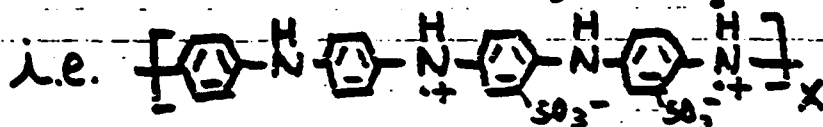
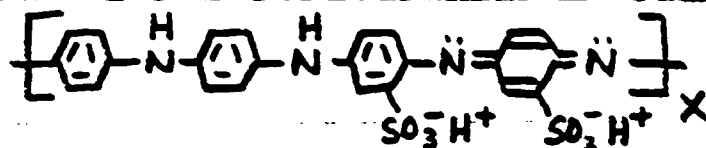


II-B-36

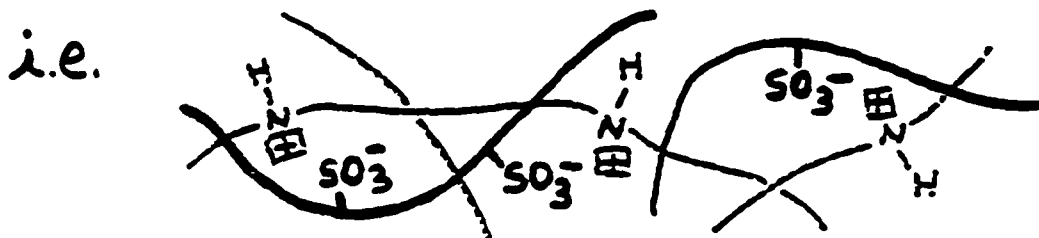
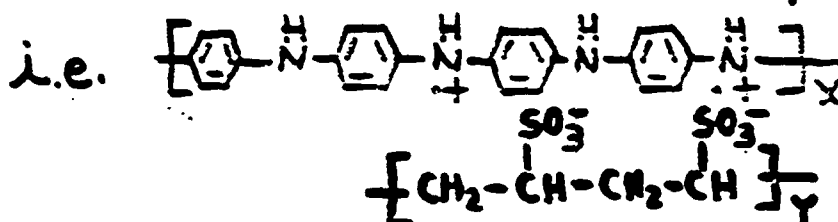
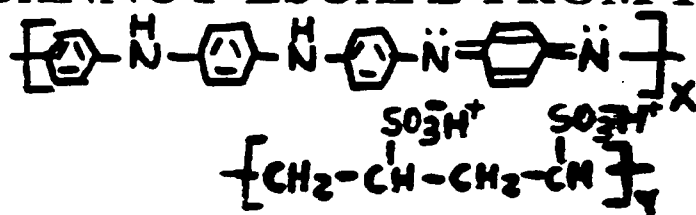
SELF-DOPED POLYANILINES

PROTONS CANNOT ESCAPE
FROM VICINITY OF POLYMER CHAIN

● BOUND TO POLYANILINE CHAIN*



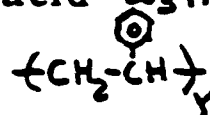
● BOUND TO POLYMERIC ANION (e.g. PolyVinylSulfonic acid) which is ENTANGLED w/ POLYANILINE CHAIN and CANNOT ESCAPE FROM IT**



INTERPENETRATING POLYMER SYSTEM ("I.P.S.")

* see Yue et. al. J. Am. Chem. Soc. 1990, 112, 2800

** similar effect with PolyStyreneSulfonic acid SO_3^-H^+

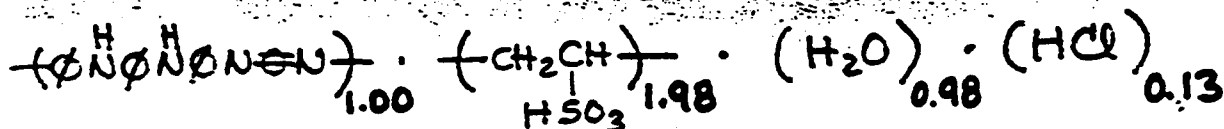


USE OF (PVS) POLY(VYNIL SULFONIC ACID)

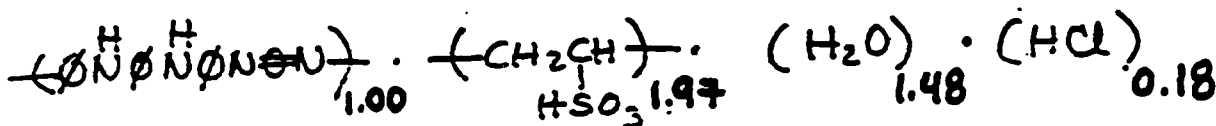
- PREPARATION OF POWDER AND THIN FILMS:
conventional prep except instead of 1M HCL
1M $-H^+SO_3^-$ from PVS acid
(from a soln. of PVS Na salt and HCl)

● ELEMENTAL ANALYSIS:

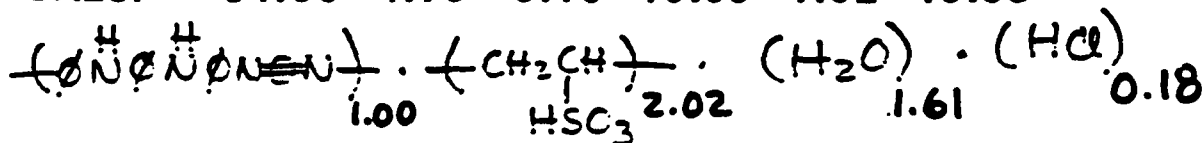
	%C	%H	%N	%S	%Cl	%O*
EXP.	56.09	4.64	9.44	10.58	0.75	18.50
CALC.	56.09	4.68	9.36	10.59	0.76	18.51



	%C	%H	%N	%S	%Cl	%O*
EXP.	55.08	4.76	9.29	10.37	1.01	19.49
CALC.	55.16	4.77	9.21	10.37	1.04	19.45



	%C	%H	%N	%S	%Cl	%O*
EXP.	54.61	4.77	9.13	10.51	1.03	19.95
CALC.	54.66	4.79	9.10	10.50	1.02	19.93

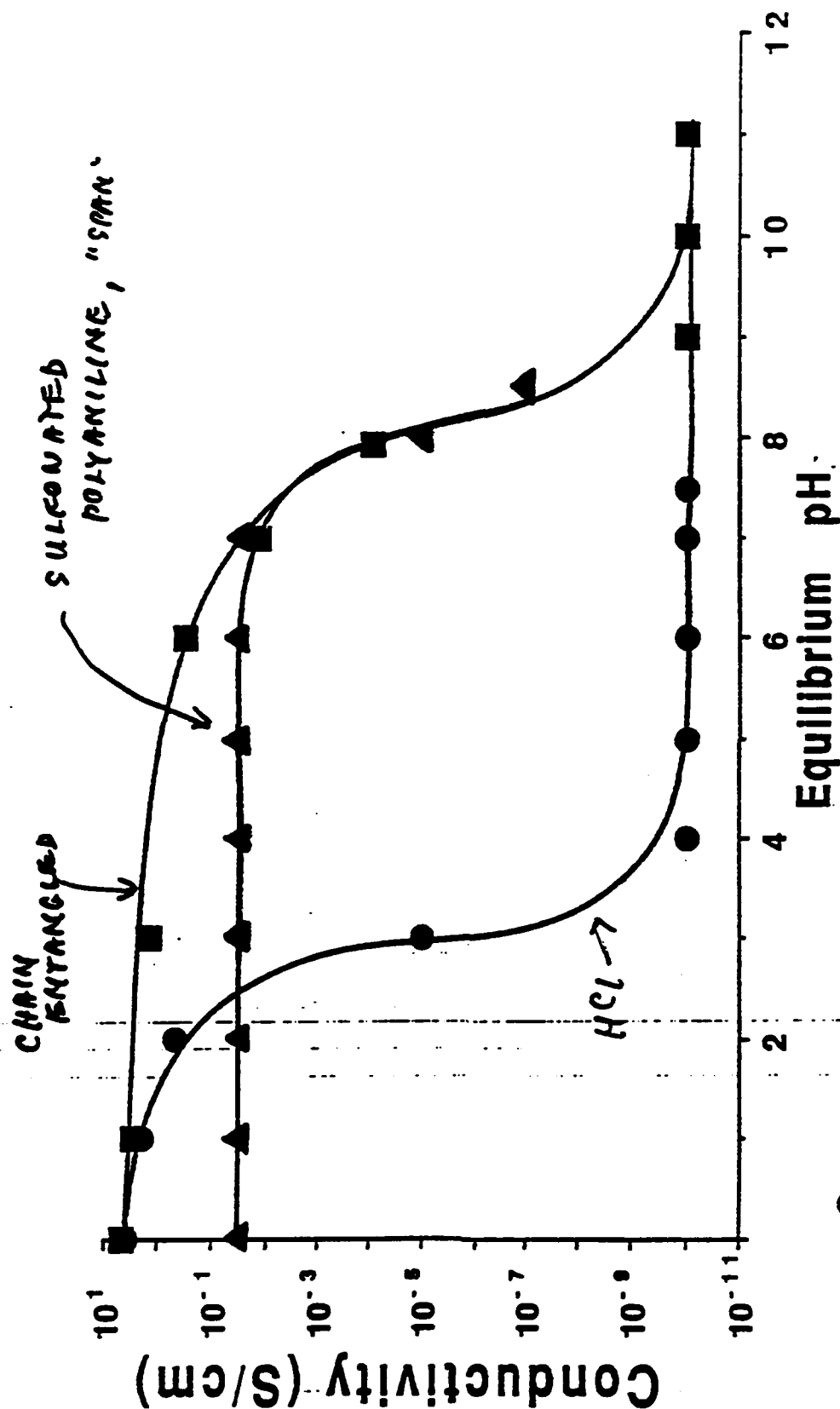


*oxygen by difference

II-B-38

● POLYANILINE DOPED WITH MONOMERIC ANION, e.g. HCl, IS UNDOPED (DEPROTONATED) BY WATER AT PH ~ 7

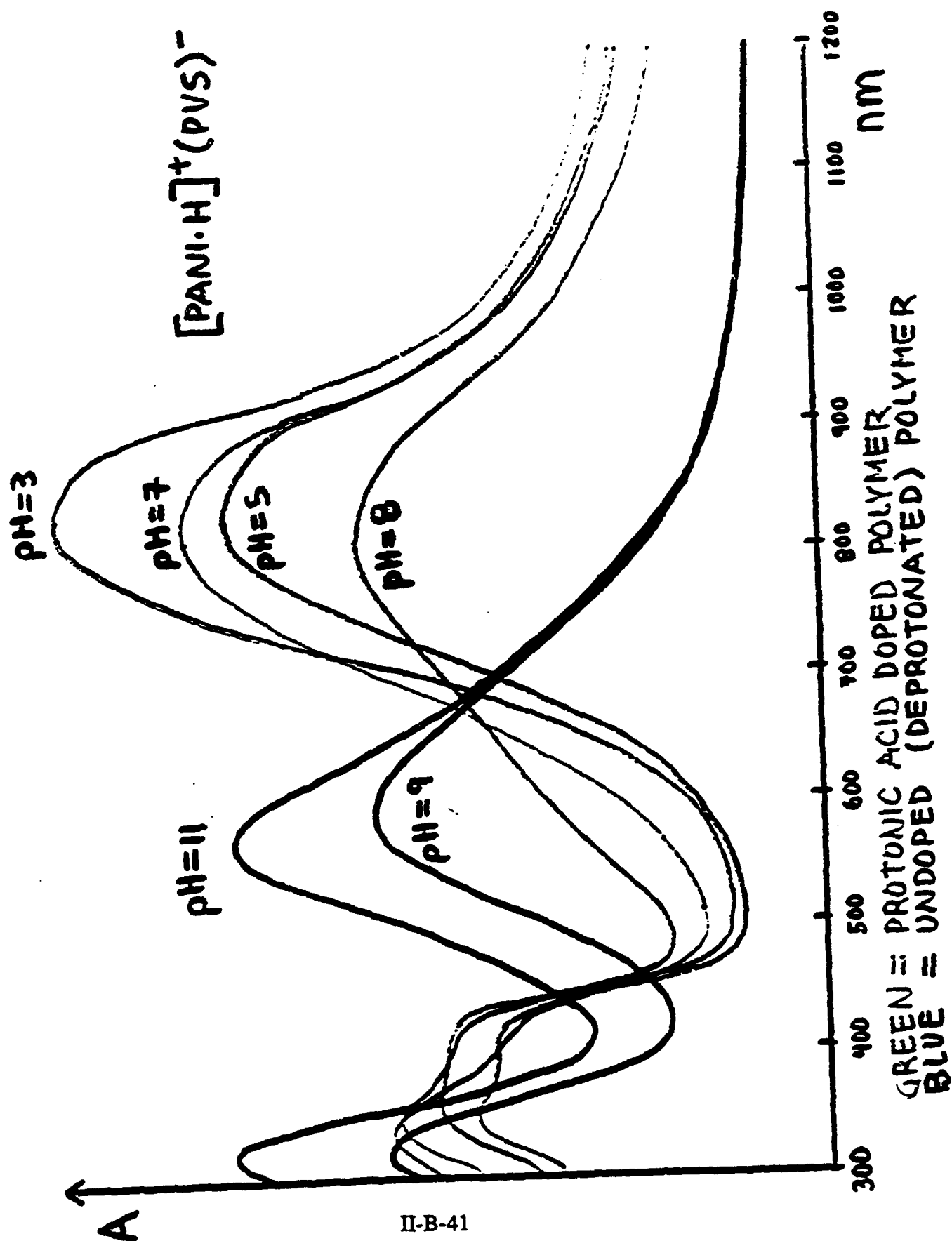
● BOTH TYPES OF SELF-DOPED POLYANILINES REMAIN DOPED (PROTONATED) AT PH ~ 7



- Protonation of emeraldine base in aq. HCl (conductivity measured in air)
- Deprotonation of emeraldine HPVS in buffers (conductivity measured in air)
- ▲ Deprotonation of sulfonated polyaniline in buffers (conductivity measured in air)

$(Em \cdot H)^+ Cl^-$ IS COMPLETELY UNDOPED (DEPROTONATED) AT $pH > \sim 4$

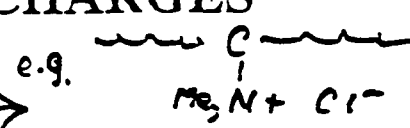
PH DEPENDENCE OF ELECTRONIC SPECTRUM



DONNAN PHENOMENA

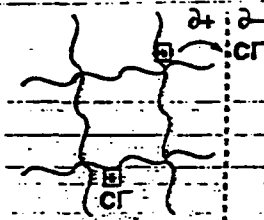
PRODUCED BY PRESENCE OF
BOTH IMMOBILE AND MOBILE CHARGES
IN A POLYMER

e.g.: conventional ion exchange resins



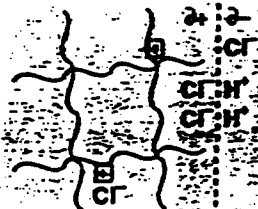
● IMMOBILE POSITIVE CHARGE

ENTROPY
EFFECT



$$\begin{aligned} \text{Donnan pot.} &= \text{pot. polym.} - \text{pot. soln.} \\ &= (\phi^+) - (\phi^-) \\ &= \text{POSITIVE} \end{aligned}$$

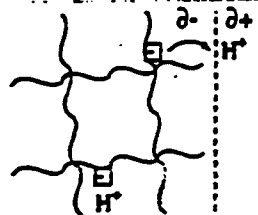
↓ add HCl



SMALLER H^+ CONC.
IN POLYMER THAN would be
the case IN THE ABSENCE
OF A DONNAN EFFECT

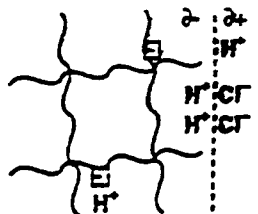
● IMMOBILE NEGATIVE CHARGE

ENTROPY
EFFECT



$$\begin{aligned} \text{Donnan pot.} &= \text{pot. polym.} - \text{pot. soln.} \\ &= (\phi^-) - (\phi^+) \\ &= \text{NEGATIVE} \end{aligned}$$

↓ add HCl

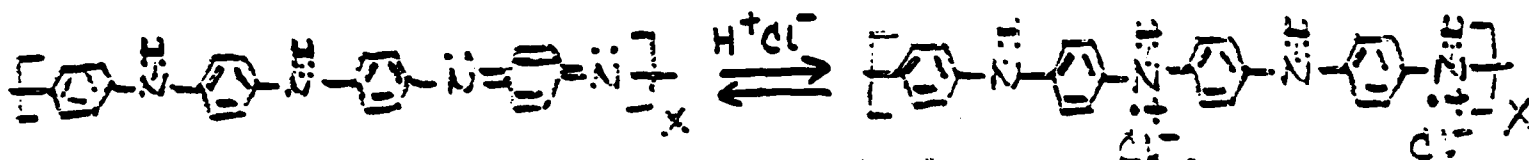


GREATER H^+ CONC.
IN POLYMER THAN would be
the case IN THE ABSENCE
OF A DONNAN EFFECT

● ADDITION OF DISSOLVED SALTS SCREENS THESE EFFECTS

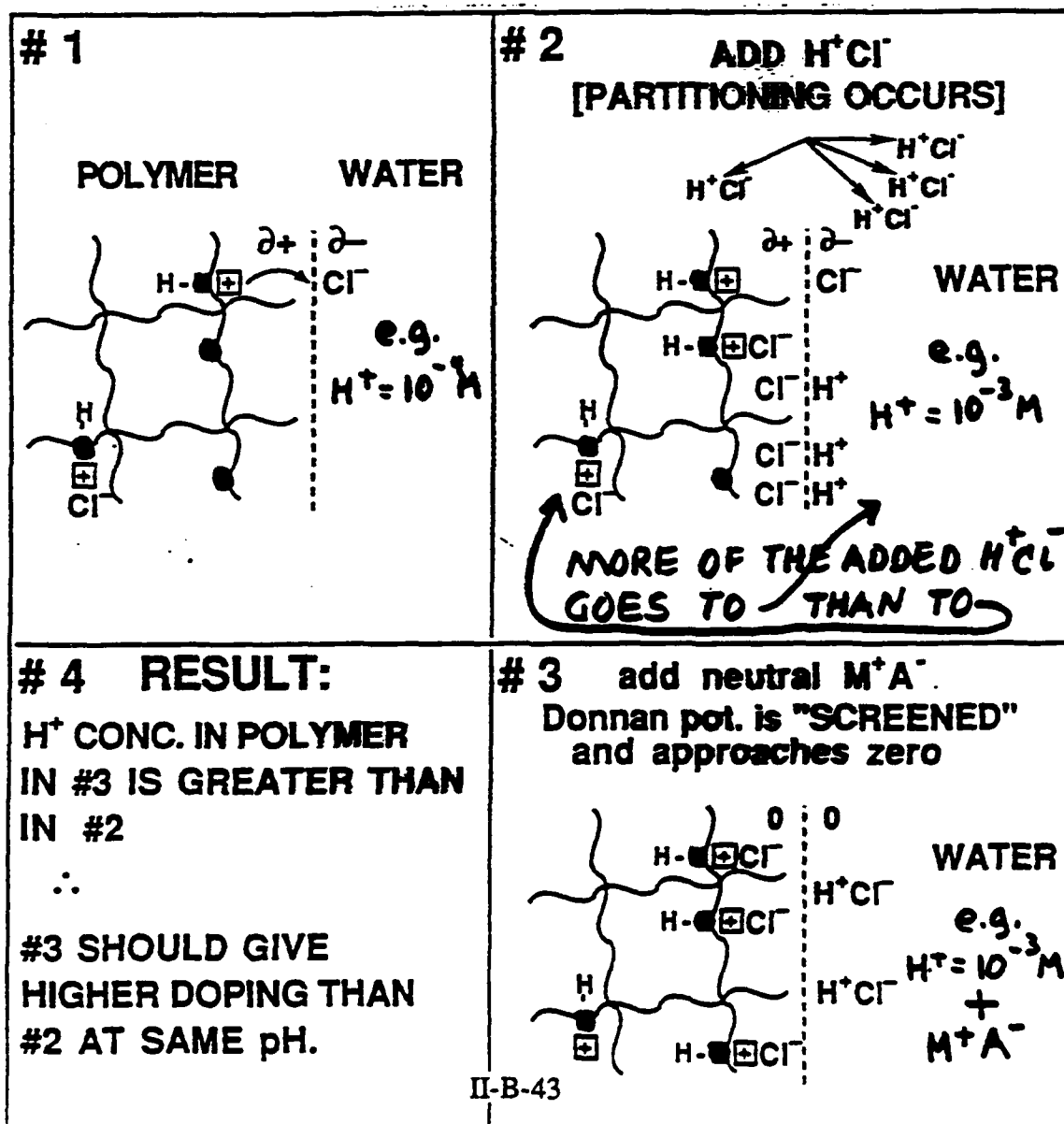
DONNAN EQUILIBRIUM EFFECTS IN DOPING OF POLYANILINE

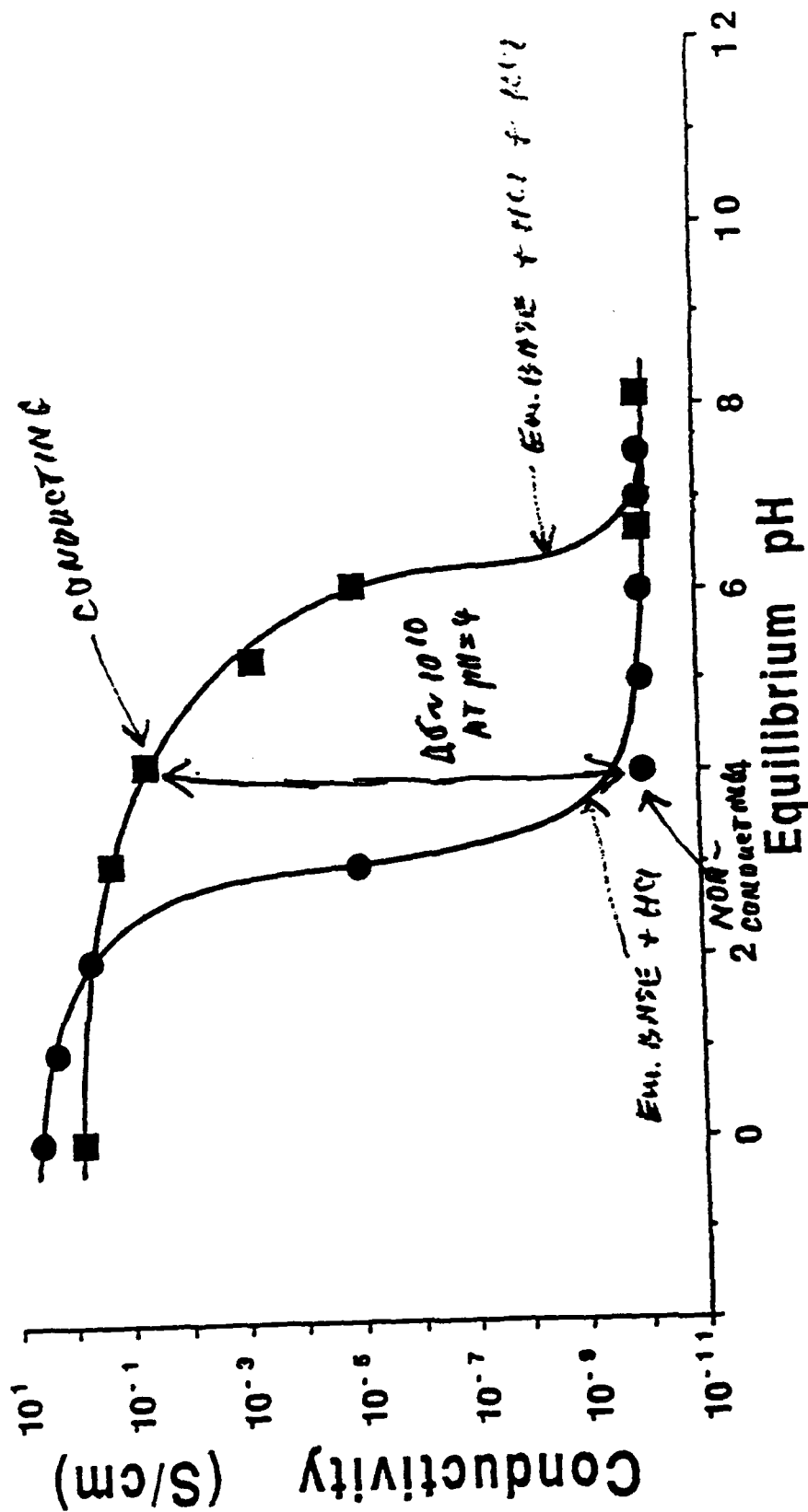
(EMERALDINE OXIDATION STATE)



+ CHARGES: [COVALENT (N-H)+ BONDS] ARE "IMMOBILE"

- CHARGES: [IONIC (N-H)+CL- BONDS] ARE MOBILE

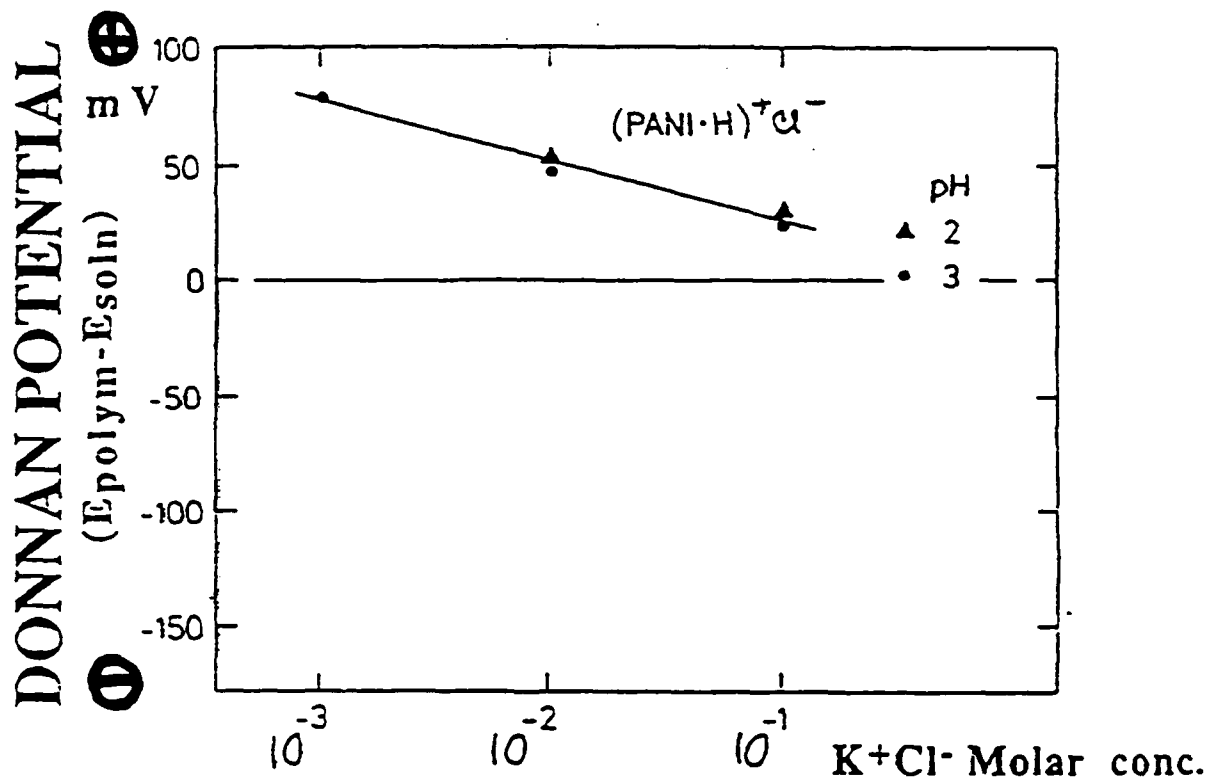




II-B-44

CASE: BUFFER SOLUTIONS GIVE DIFFERENT CONDUCTIVITIES
AT THE SAME pH THAN PURE ACID SOLUTIONS !!

DONNAN POTENTIAL MEASUREMENTS ON (PANI·H)⁺Cl⁻ *



(PANI·H)⁺Cl⁻
SHOWS A POSITIVE DONNAN POTENTIAL
(which decreases in magnitude when the ionic
strength is increased)

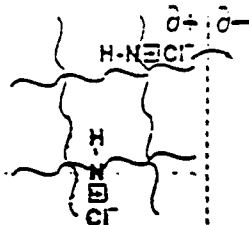
∴ IT CONTAINS "IMMOBILE"
POSITIVE CHARGES

* WITH PROF. KARL DOBLHOFFER,
FRITZ - HABER INST., BERLIN

II-B-45

this has described...

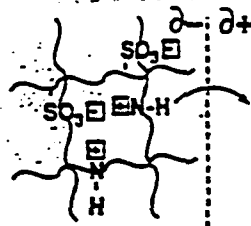
(I) **Em·HCL SYSTEM** which has a
POSITIVE DONNAN POTENTIAL



i.e.: the positive charges are much less
mobile than the negative Cl^- 's

can also have the REVERSE, i.e.:

(II) **Em·HPVS SYSTEM** which has a
NEGATIVE DONNAN POTENTIAL*

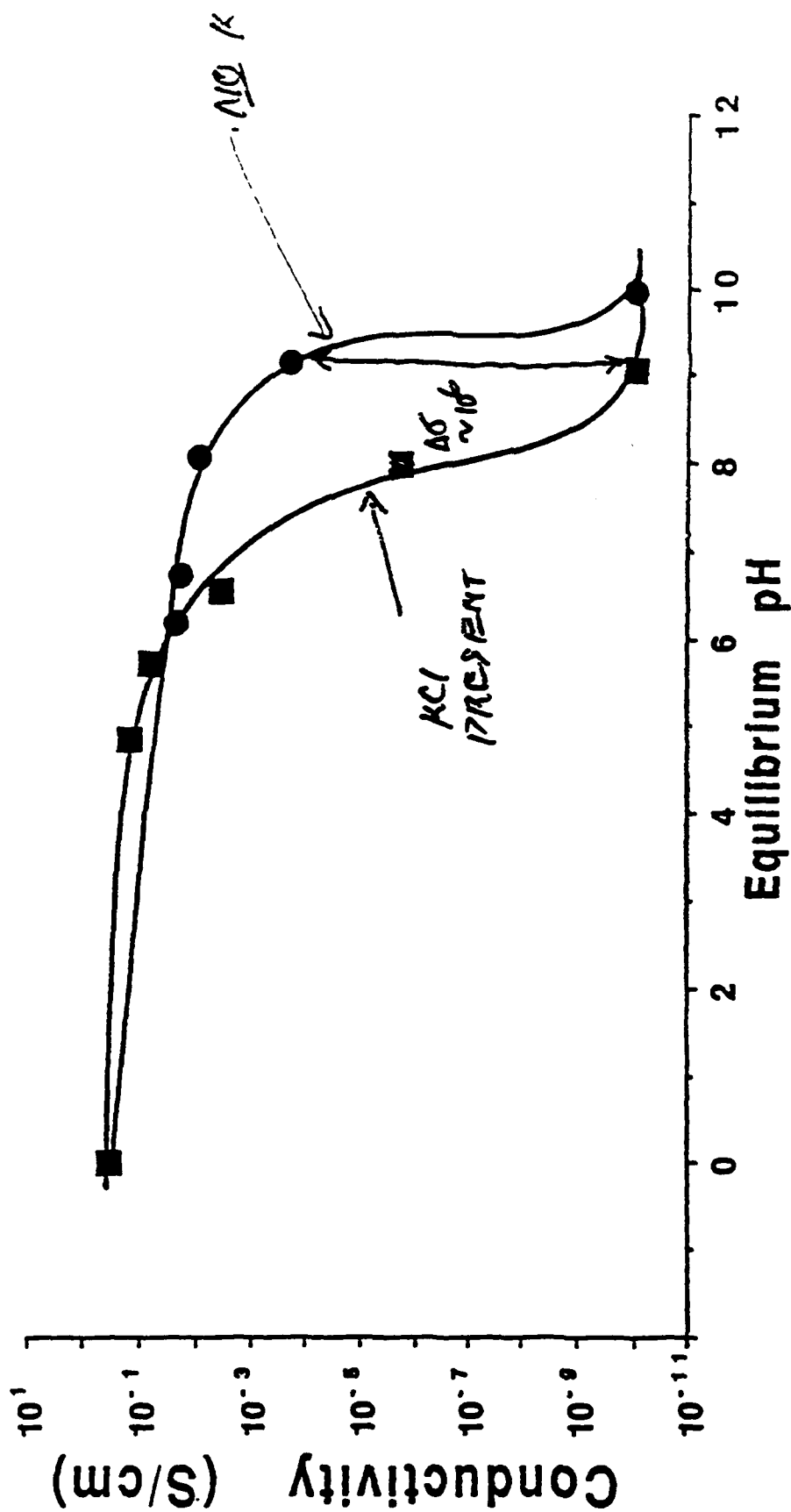


∴ all PARTITIONING EFFECTS are the
REVERSE of (I), i.e.:

● **H^+ CONC. IN THE Em·HPVS SYSTEM
IS GREATER THAN** would be the case
IN THE ABSENCE OF A DONNAN EFFECT

● **ADDITION OF SALT DECREASES THE
 H^+ CONC. IN THE POLYMER PHASE**

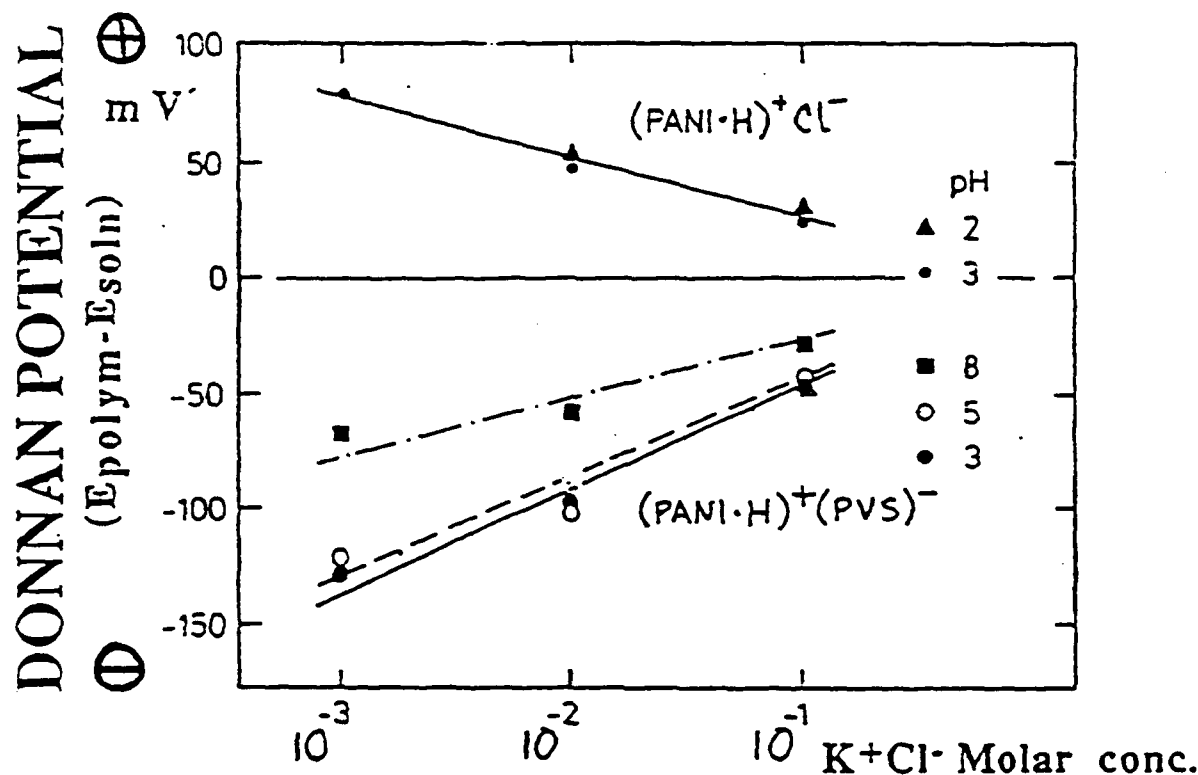
* the negative PVS^- is completely immobile,
∴ the negative charge becomes dominant effect
since the small mobility of the H^+ in $(\text{N-H})^+$
becomes important



- Deprotonation of emeraldine.HPVS in aq. HCl or (NH₄)OH (conductivity measured in dry box)
- Deprotonation of emeraldine.HPVS in aq. HCl or (NH₄)OH + 0.5M KCl (conductivity measured in dry box)

HPVS = polyvinylsulfonic acid

DONNAN POTENTIAL MEASUREMENTS: $(\text{PANI}\cdot\text{H})^+(\text{PVS})^-$ *



$(\text{PANI}\cdot\text{H})^+(\text{PVS})^-$
SHOWS A NEGATIVE DONNAN POTENTIAL
(which decreases in magnitude when the ionic strength is increased)

∴ IT CONTAINS IMMOBILE
NEGATIVE CHARGES

* WITH PROF. KARL DOBLHOFFER,
FRITZ - HABER INST., BERLIN
II-B-48

CONCLUSION

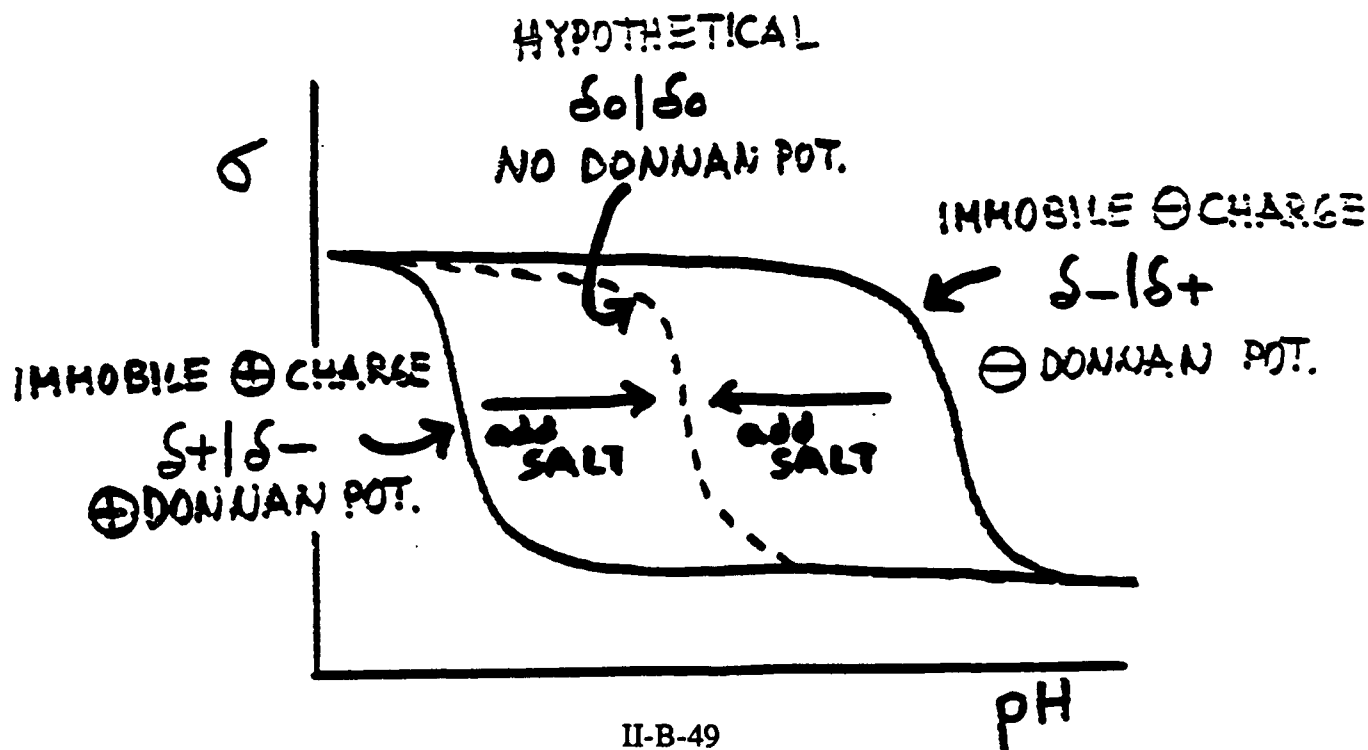
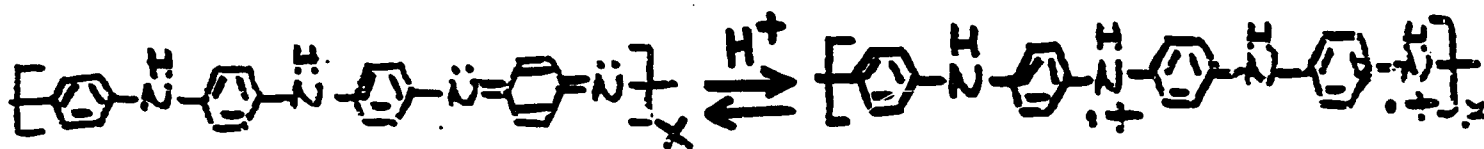
∴ PARTITIONING OF H^+
between the polymer and the solution

● DEPENDS ON THE DONNAN POTENTIAL

and

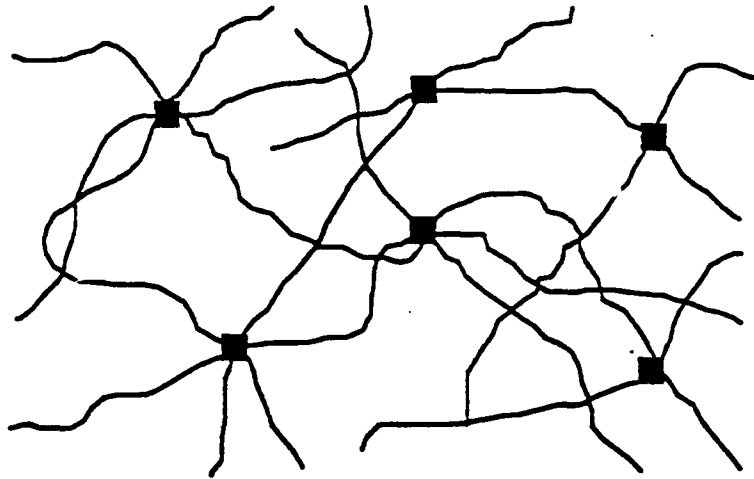
● DETERMINES THE EXTENT OF PROTONIC
ACID DOPING OF THE POLYANILINES

by shifting the equilibrium:



POLYANILINE
(EMERALDINE BASE)
GELS

GEL: A state of matter intermediate between a solid and a liquid



■ = crosslinks between chains.

can be either: chemical bonds

or: physical, i.e. microcrystalline regions

Gels Can swell, sometimes enormously, when placed in certain liquids (in which they are insoluble).

Synthesis of Polyaniline Gels

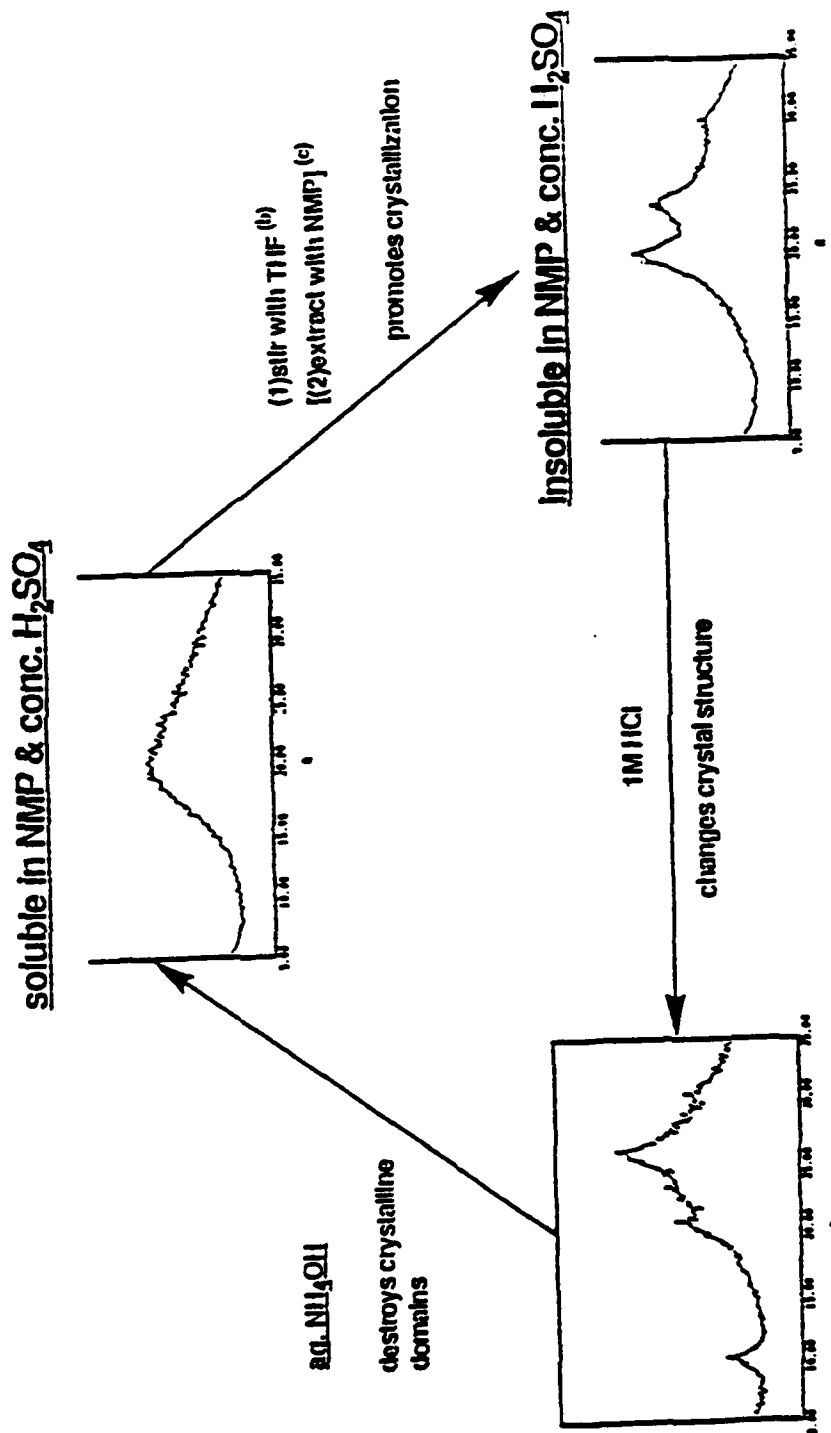
- . 20 wt % emeraldine base "solution" in NMP
- . stir for ~15 min. until the "solution" becomes very viscous
- . pour on to a substrate or into a container
- . after ~5-10 min. congeals to "Jelly-like" material*
- . hold at ~60 °C (N₂) for 1.5 hrs.
- . leave at room temperature overnight (crude gel*)
- . peel film off the substrate and extract soluble portion (~21 wt %) with NMP until NMP is colorless
- . emeraldine base gel (contains > 50 wt % NMP)
swellable in NMP, but not soluble in NMP

* still contains some soluble polymer

- $\bar{M}_n \sim 25,000$; 3% solution, GELATION OCCURS ~12 WEEKS
- WITH $\bar{M}_n \sim 127,000$; 3% solution, GELATION OCCURS IN ~24 HOURS

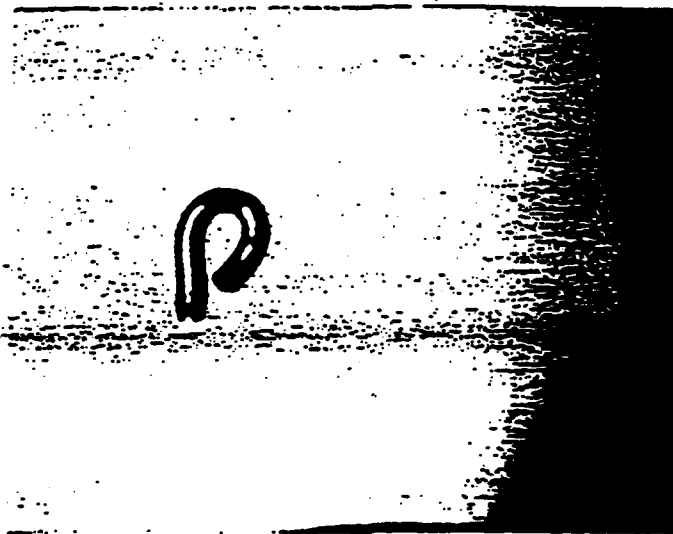
Solubility Dependency on The Degree of Crystallinity of Emeraldine Base ^(a)

(X-ray diffraction data)



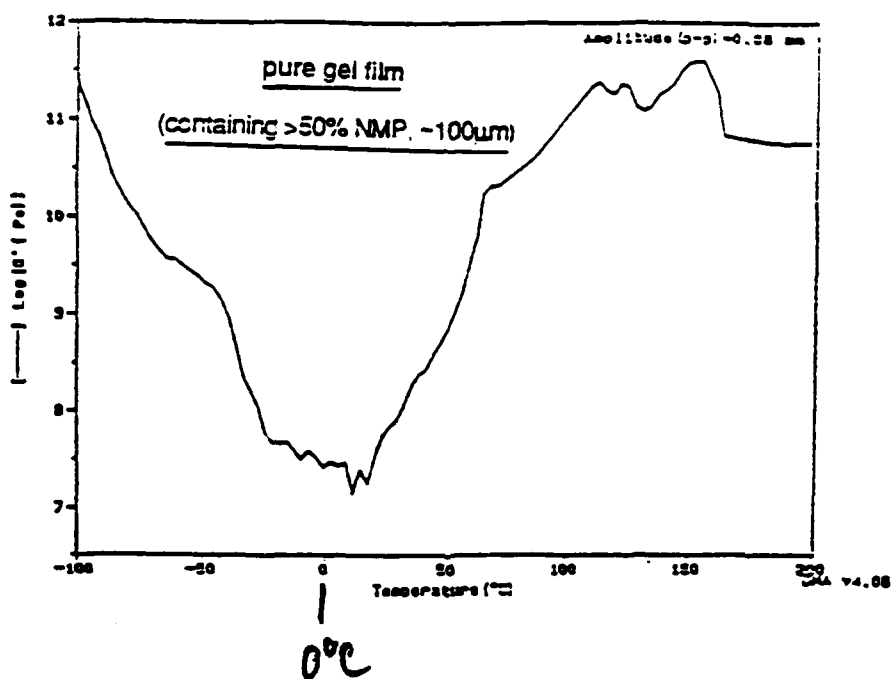
- (a) Tang et al., *Brit. Am. Phys. Soc.*, 1909, 34, 503 ; MacDiarmid et al., *Faraday Discuss. Chem. Soc.*, 1909, 88, 317
 (b) polymer chains become solvated, resulting in chain mobility, promoting crystallization.
 (c) only needed on 1st cycle i.e. when starting with "as-synthesized" emeraldine base.

Polyaniline Gel

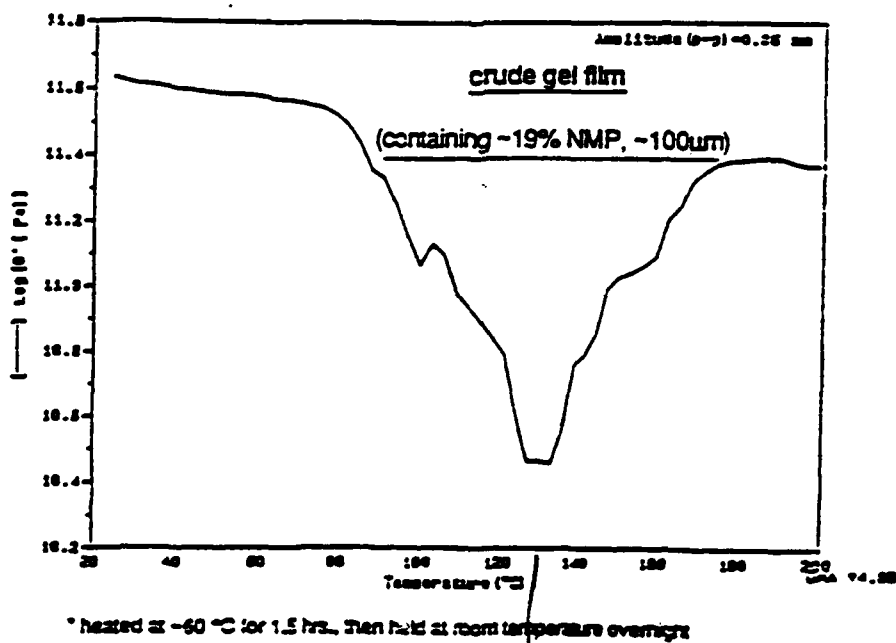


- very flexible at room temperature
- some forms of polyaniline (EB) gels (films or rods) are elastomeric

DMA of Emeraldine Base Gel Film

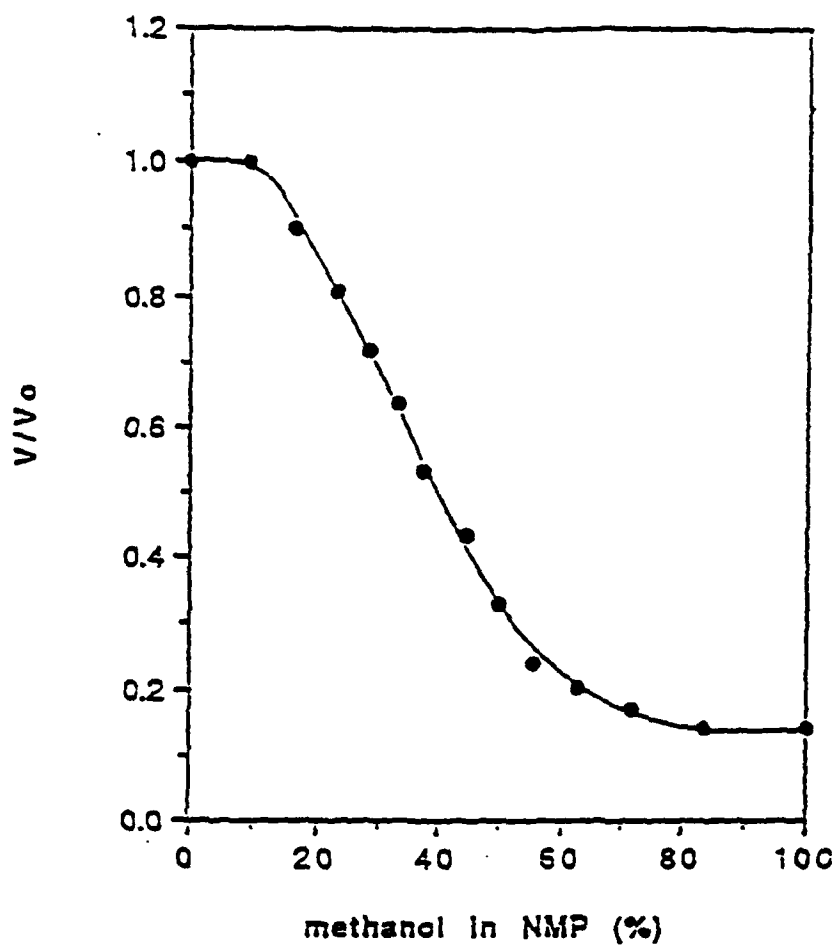


DMA of Emeraldine Base Film *



130°C

Dependency of Volume Shrinkage Ratio of Emeraldine Base
Gel Film on CH_3OH Concentration in NMP

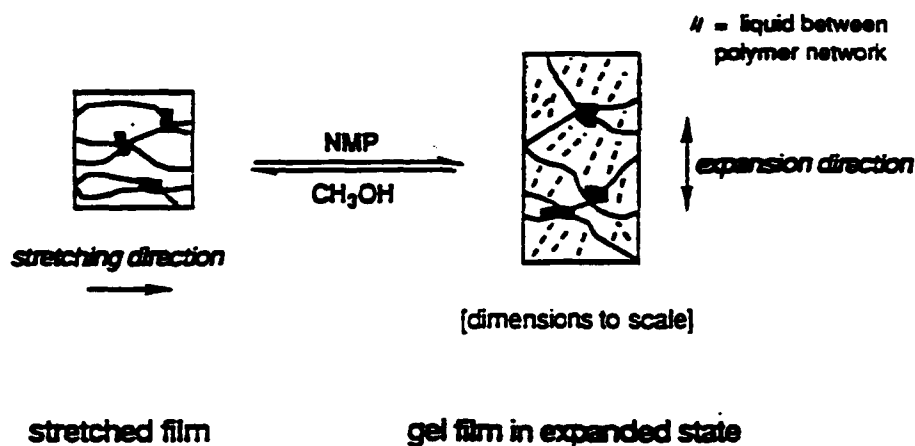


V : volume of gel film in NMP solution with varied concentration
of CH_3OH

V_0 : volume of gel film in pure NMP

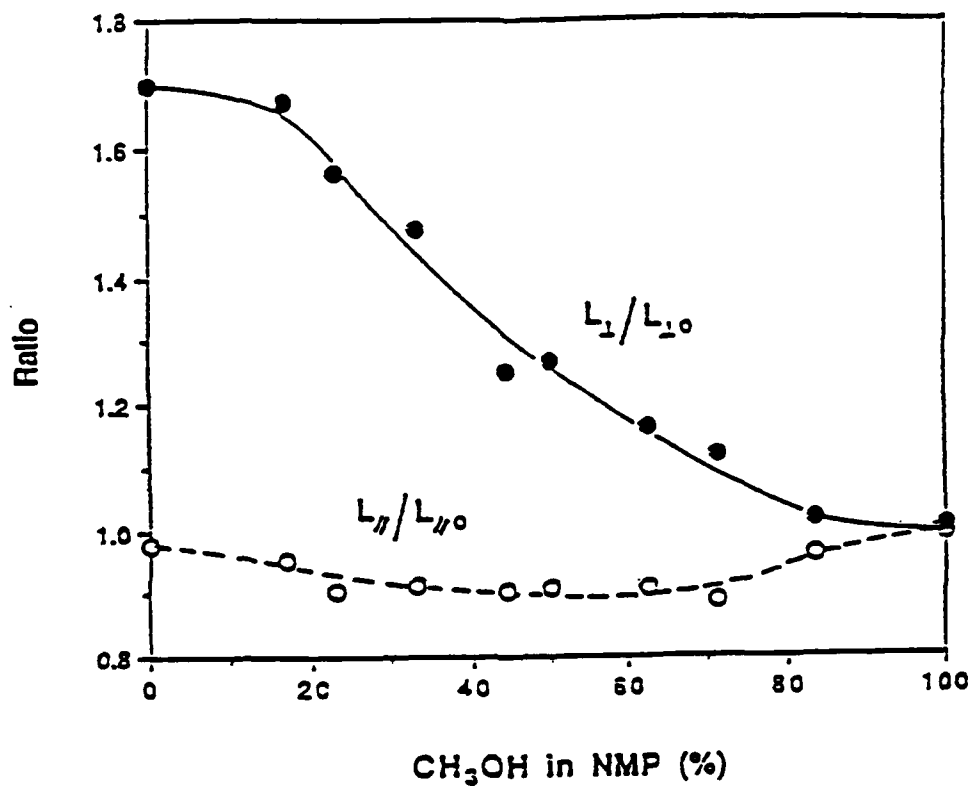
Anisotropic Expansion of Stretch-Aligned Gel Film (A "Shape - Memory" Polymer)

- emeraldine base film *
- thermally stretched at $\sim 100^\circ\text{C}$ (N_2) to 1.5 times its original length ($L/L_0 \sim 1.5$) and cut in to the shape of a square
- immediately immersed in NMP
- extract NMP soluble portion with NMP until NMP is colorless; film expands in the direction perpendicular to the stretching direction



* heated at -60°C for 1.5 hrs., then held at room temperature overnight

Change in Dimensions of Stretch-Aligned Emeraldine Base Film
($L/L_0 \sim 1.5$) As a Function of NMP/CH₃OH Concentration



L_{10} : initial length in the direction perpendicular to stretching direction

L_1 : length in the direction perpendicular to stretching direction in NMP/CH₃OH

L_{20} : initial length in the direction parallel to stretching direction

L_2 : length in the direction parallel to stretching direction in NMP/CH₃OH

Evidence for Physical (Microcrystallite) Crosslinking in Polyaniline Gels

I: Solubility (Doping and Dedoping) Study

II: Crystallinity/Swellability Studies

I: Solubility (Doping and Dedoping) Study

emeraldine base gel film in expanded state in NMP

↓
immerse in CH_3OH , and dry
in vacuum at -25°C

emeraldine base gel in shrunken state

↓
1) dope with 1M HCl; 2) dedope with 0.1M NH_4OH ;
3) dry in vacuum; 4) dissolve in NMP

→ emeraldine base/NMP solution

emeraldine base fragments

↓
repeat procedure 1-4

→ emeraldine base/NMP solution

↓
repeat procedure 1-4

→ emeraldine base/NMP solution

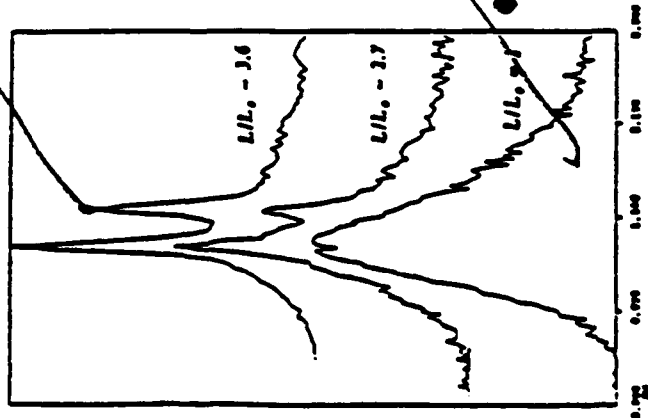
all dissolves

CONCLUSION:

The crosslinking consists of microcrystalline domains. As shown earlier, doping and dedoping destroys the crystalline domains and makes it soluble in NMP.

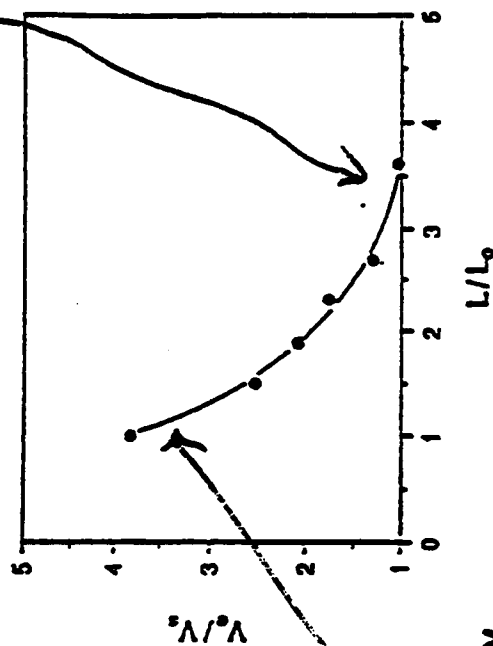
II: Crystallinity/Swellability Studies

X-Ray diffraction of Stretched Film



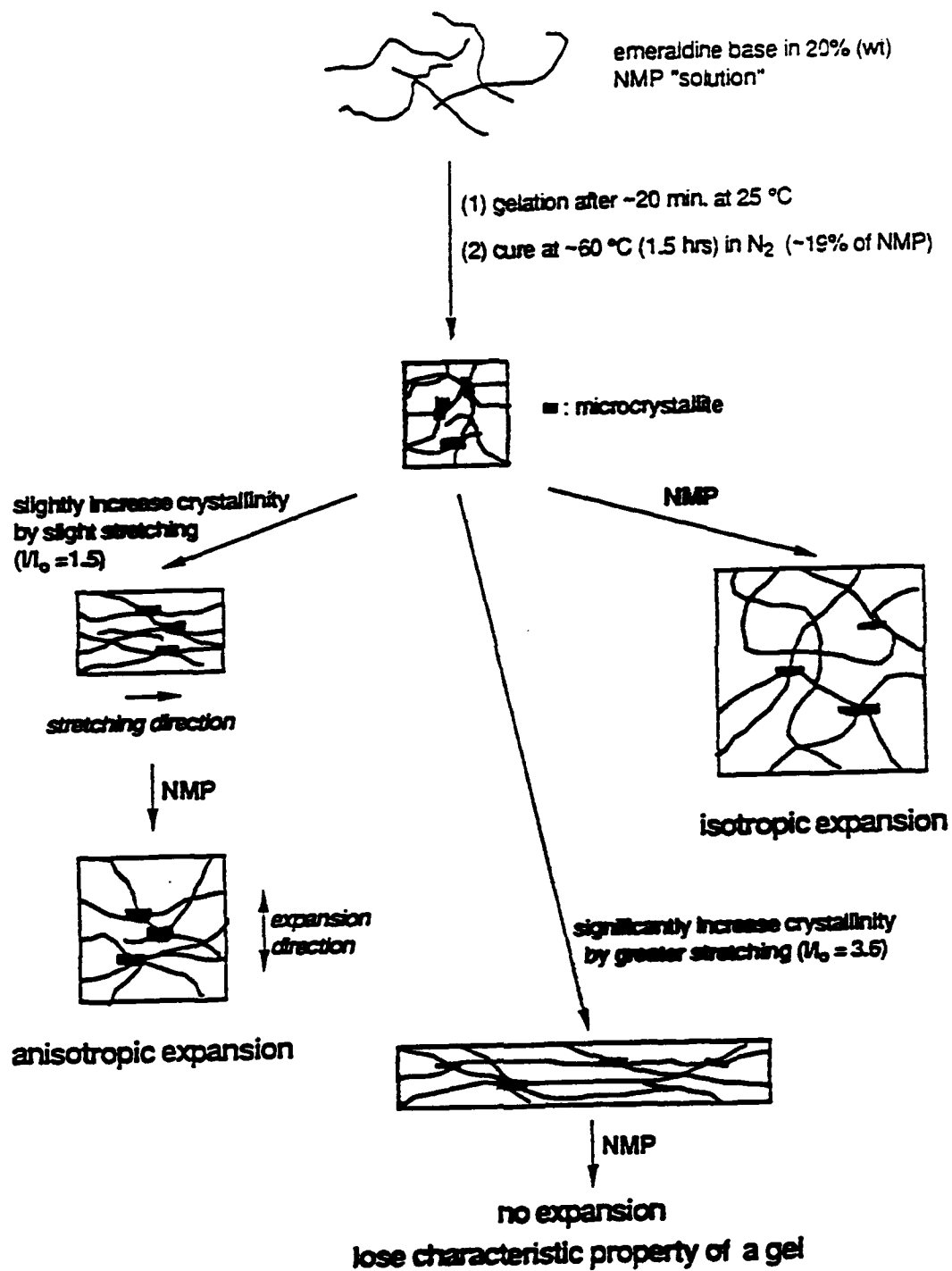
• SLIGHTLY
CRYSTALLINE
• MUCH
SWELLING

Expansion Ratio vs. Drawn Ratio of emeraldine base film

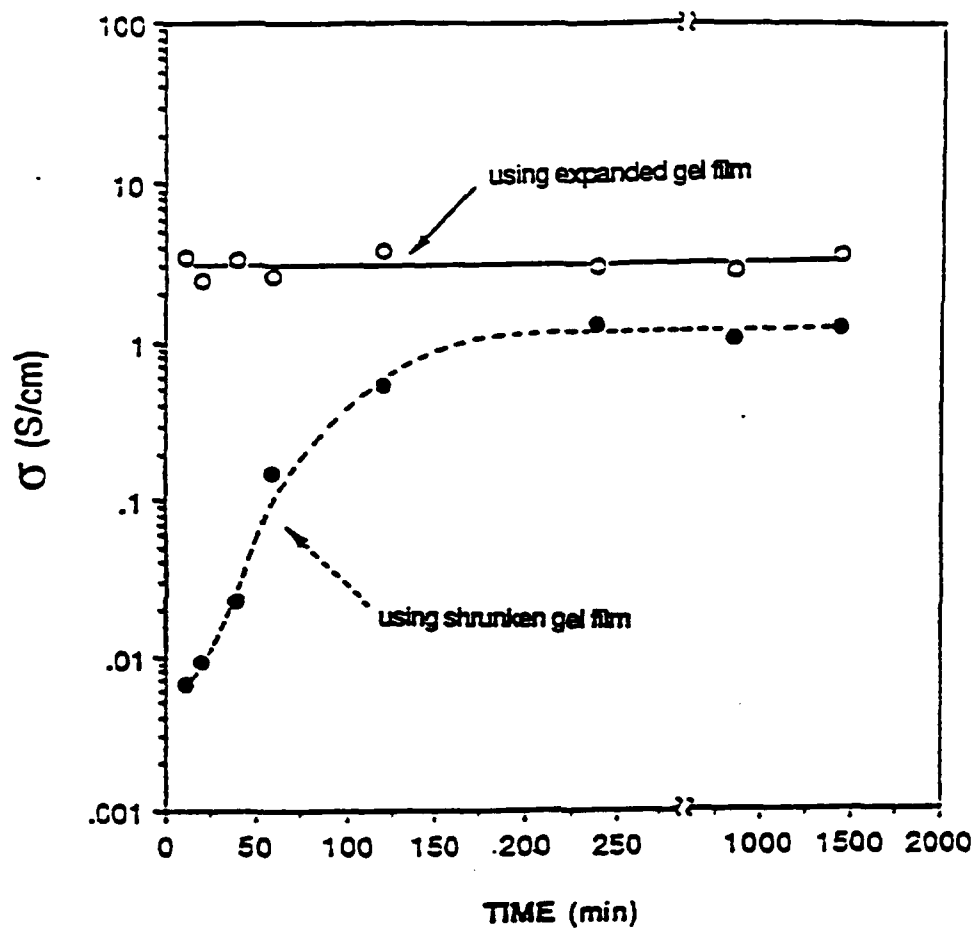


• VERY CRYSTALLINE
• NO SWELLING

Mechanism of Emeraldine Base Gel Formation



Dependancy of Conductivity of Gel Film on Doping Time^(a)



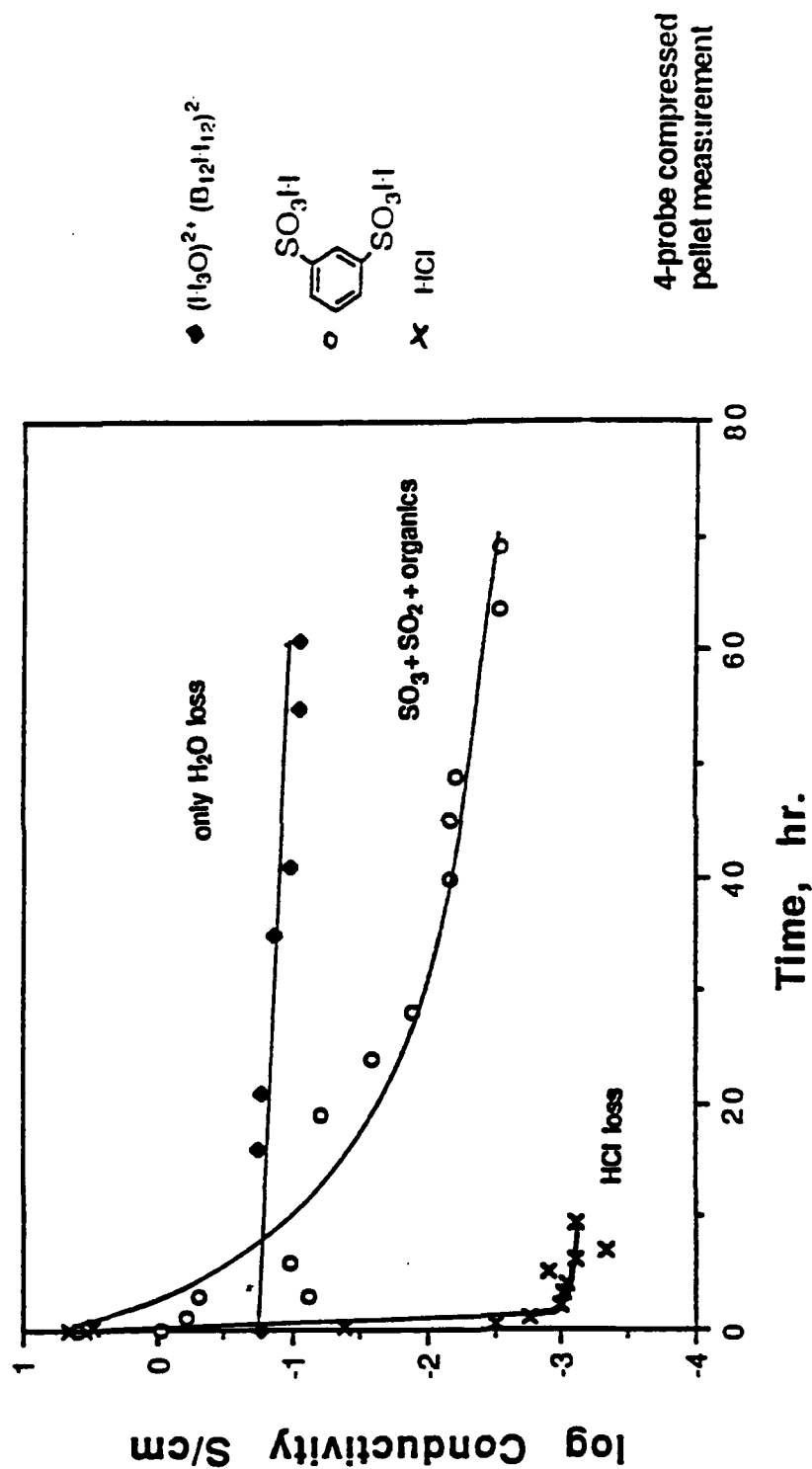
a) dopant: pentadecafluorooctanoic acid, $\text{CF}_3(\text{CF}_2)_6\text{COOH}$
 0.5M in 1:1 $\text{CH}_3\text{OH}/\text{H}_2\text{O}$

σ: 4 probe on dry film

b) open circle: large shrinkage during doping
 filled circle: no shrinkage during doping

**THERMALLY AND OXIDATIVELY
STABLE CONDUCTING
POLYANILINE SALTS**

Pellet Conductivity vs. Time for Polyaniline Salts Heated in Vacuum at ~ 188°C

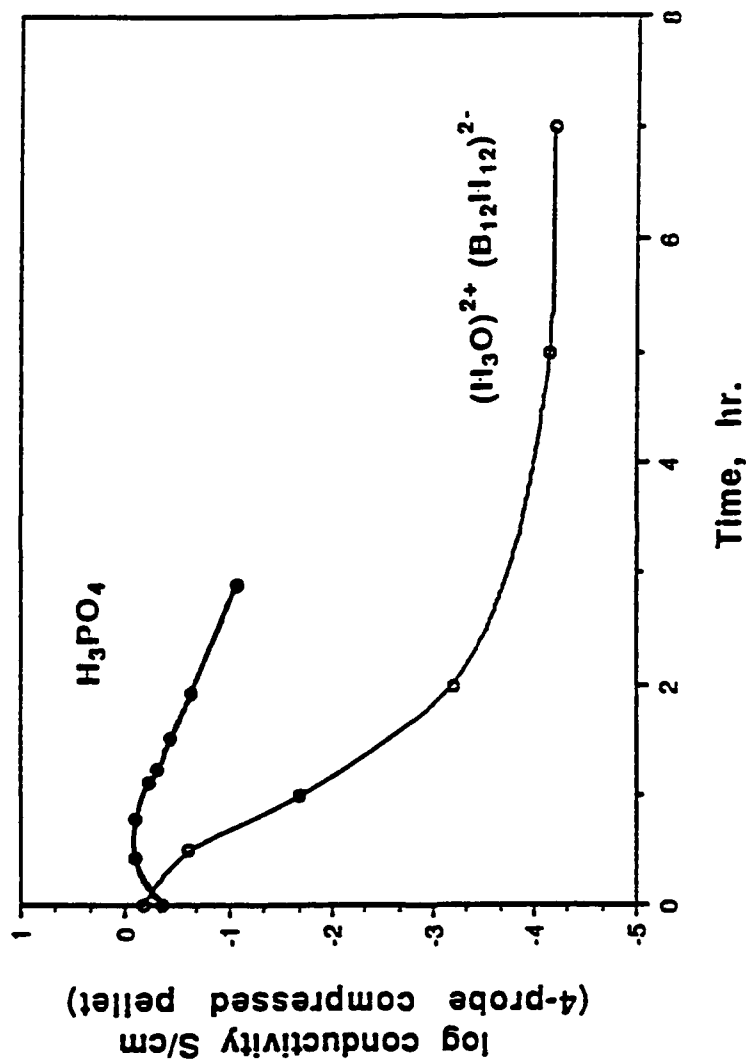


II-B-65

Each data point represents a different compressed pellet

Other factors being equal, decreased volatility of dopant acid increases thermal stability

Conductivity vs. Time for Polyaniline Salts Heated in air at 235°C



Each data point represents a different compressed pellet

The H_3PO_4 doped salt exhibits good oxidative stability at elevated temperature over the heating time studied

PROCESSING
OF
POLYANILINE

**THE INTRINSIC PROPERTIES OF CONDUCTING POLYMERS
CAN ONLY BE DETERMINED BY PROCESSING**

CAN CAST LARGE FLEXIBLE FREE - STANDING COPPERY -
COLORED FILMS ($\approx 6'' \times 6''$) OF POLYANILINE (EMERALDINE
BASE; $\sigma \approx 10^{-9}$ S/cm) FROM N.M.P. SOLUTION ($\approx 1-2$ wt.%)



1 M aq. HCl

EMERALDINE.HCl
($\sigma \approx 1 - 5$ S/cm) *

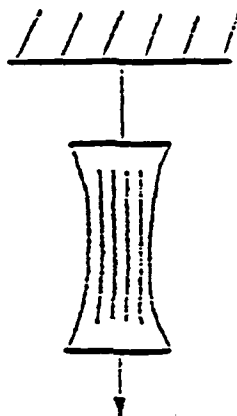
PURPLE, FLEXIBLE, FREE - STANDING FILMS

* NO CHANGE IN σ SINCE "ADRIATIC CONFERENCE ON 1-D
CONDUCTORS," TRIESTE, JUNE 30 — JULY 3, 1987).

THERMAL PROCESS FOR STRETCH - ORIENTATION OF POLYANILINE

EMERALDINE BASE CONTAINING ≈ 15 WT. % N. M. P.

FILMS HELD UNDER TENSION AND RAPIDLY HEATED
TO $\approx 120^{\circ}\text{C}$ IN INERT ATMOSPHERE.



TENSION

- DOPE IN 1M HCl
- FOR $l/l_0 = 4$; $\sigma_{\parallel} \approx 10^2$ S/cm
- $(\sigma_{\parallel} / \sigma_{\perp}) \approx 10$
- (σ OF POWDER AND NON - STRETCHED FILM ≈ 3 S/cm)
- WATER ACTS AS A SYNERGISTIC DOPANT WITH HCl
- σ GREATLY DEPENDENT ON EXTENT OF DRYING
- $\sigma \approx 80$ S/cm (DYNAMIC VACUUM FOR 48 HOURS)
- $\sigma \approx 300$ S/cm AFTER EXPOSURE TO WATER VAPOR

111

4:1

35:1

3:1

II-B-70

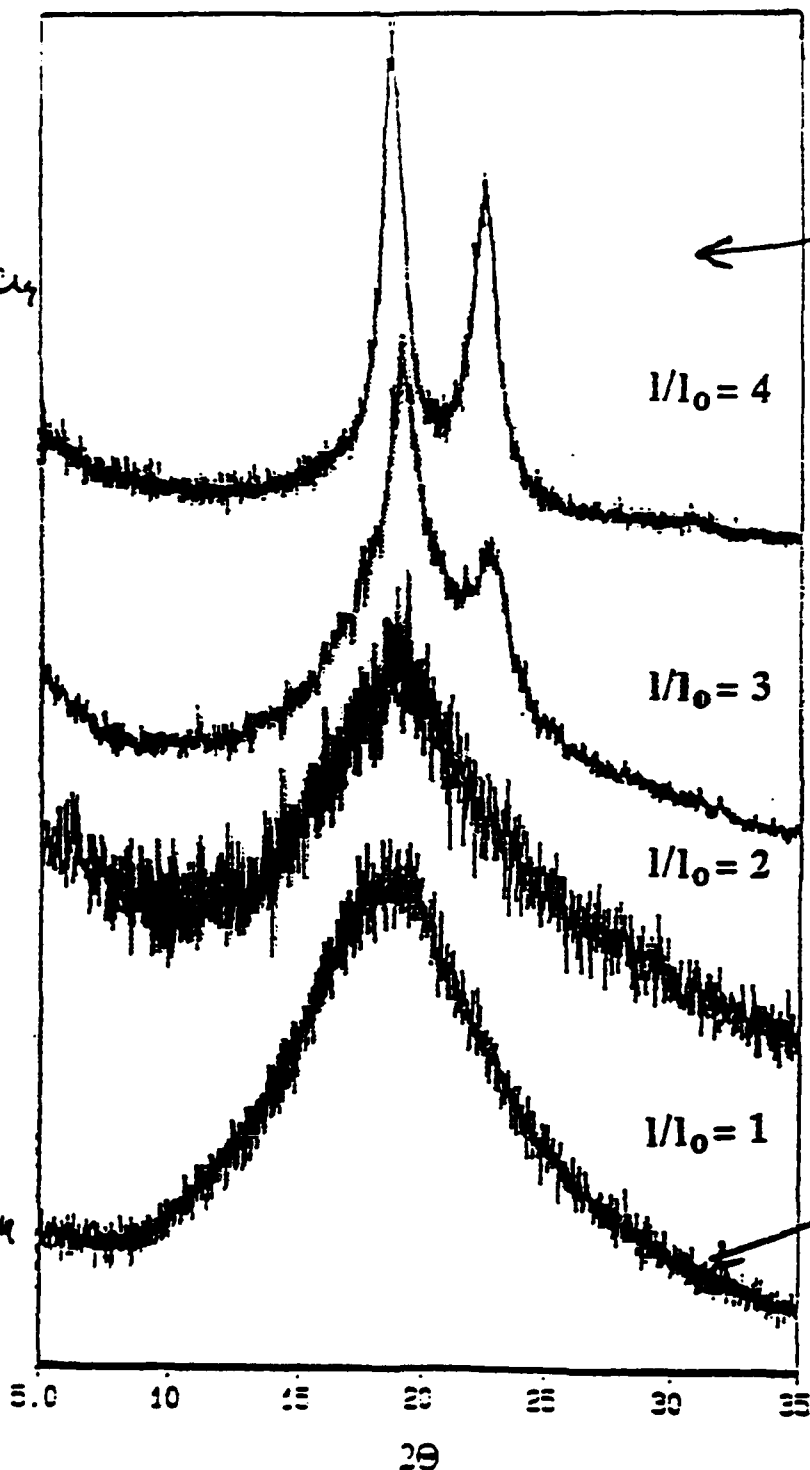
5
AFTER
DOPING
IN HCl

$G \sim 10^2 \text{ g/cm}$

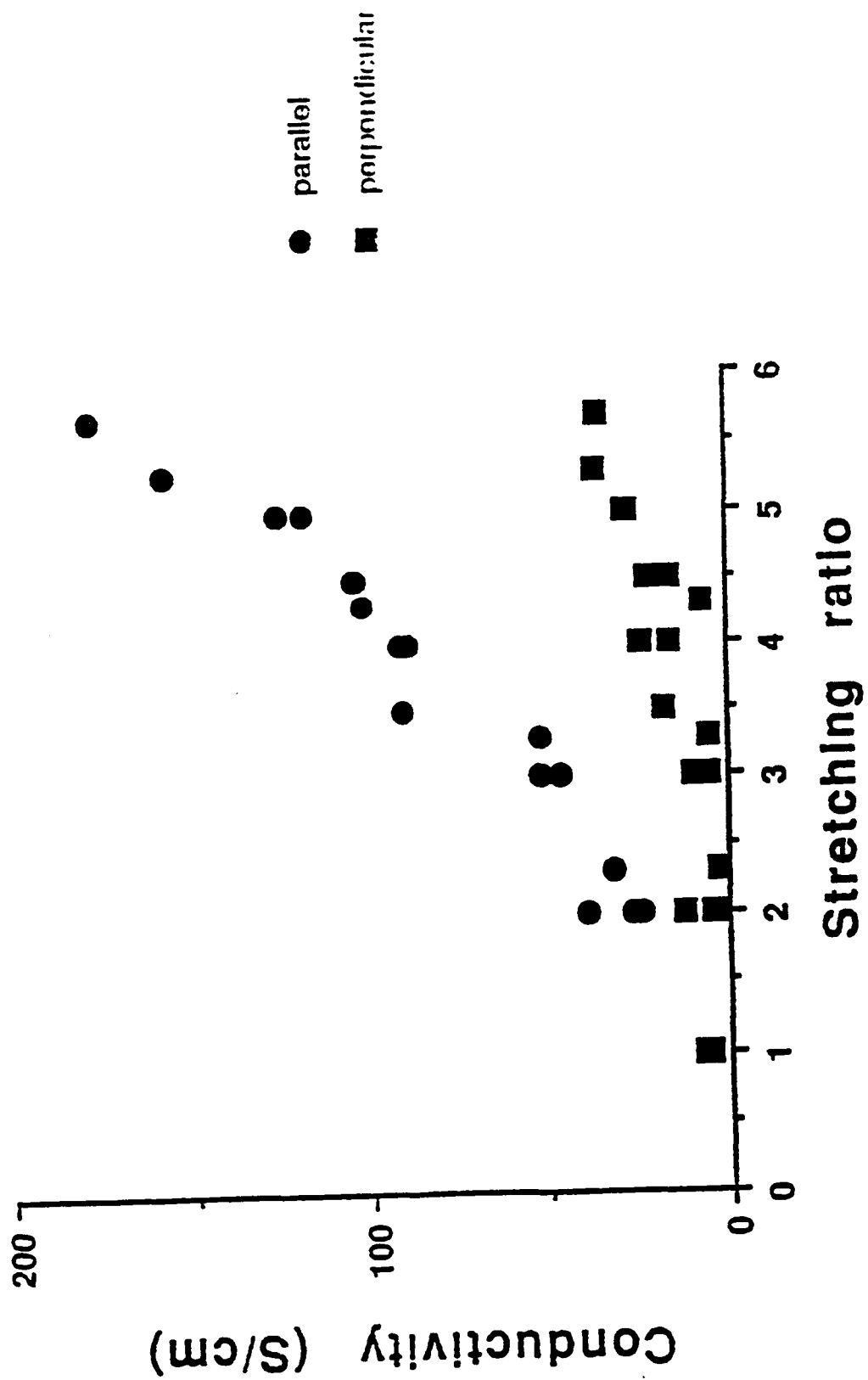
← SOLUBLE
IN N.M.P.

$G \sim 3 \text{ g/cm}$

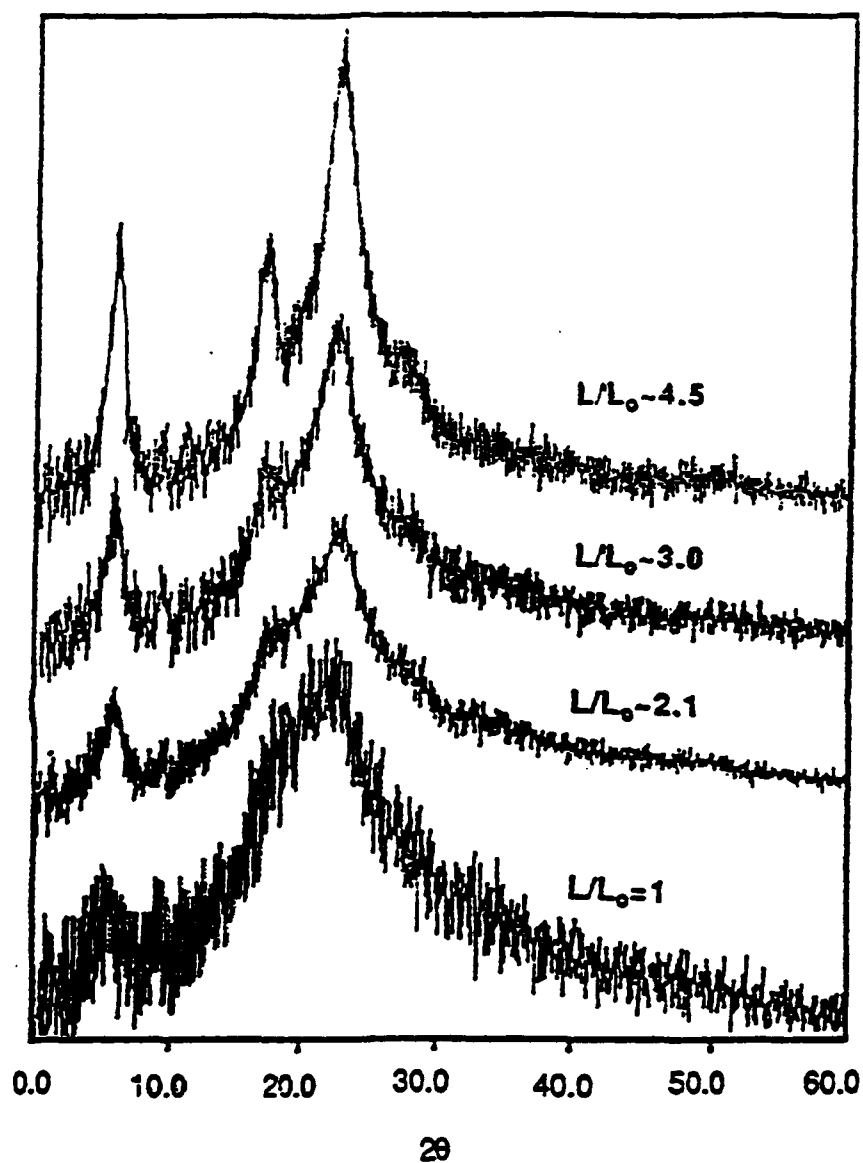
ALMOST
COMPLETELY
SOLUBLE IN
N.M.P.



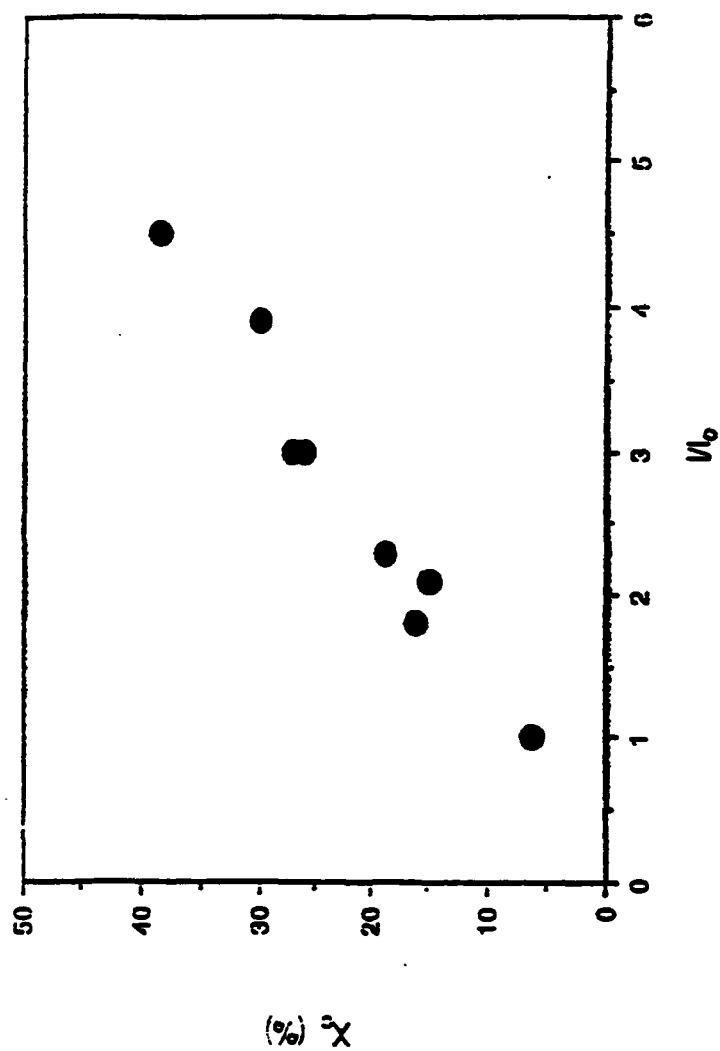
X-Ray Diffraction Spectra of Ribbons of
Emeraldine Base of Increasing Draw Ratio.
(l/l_0 ; l = final length; l_0 = original length before stretching)
II-B-71



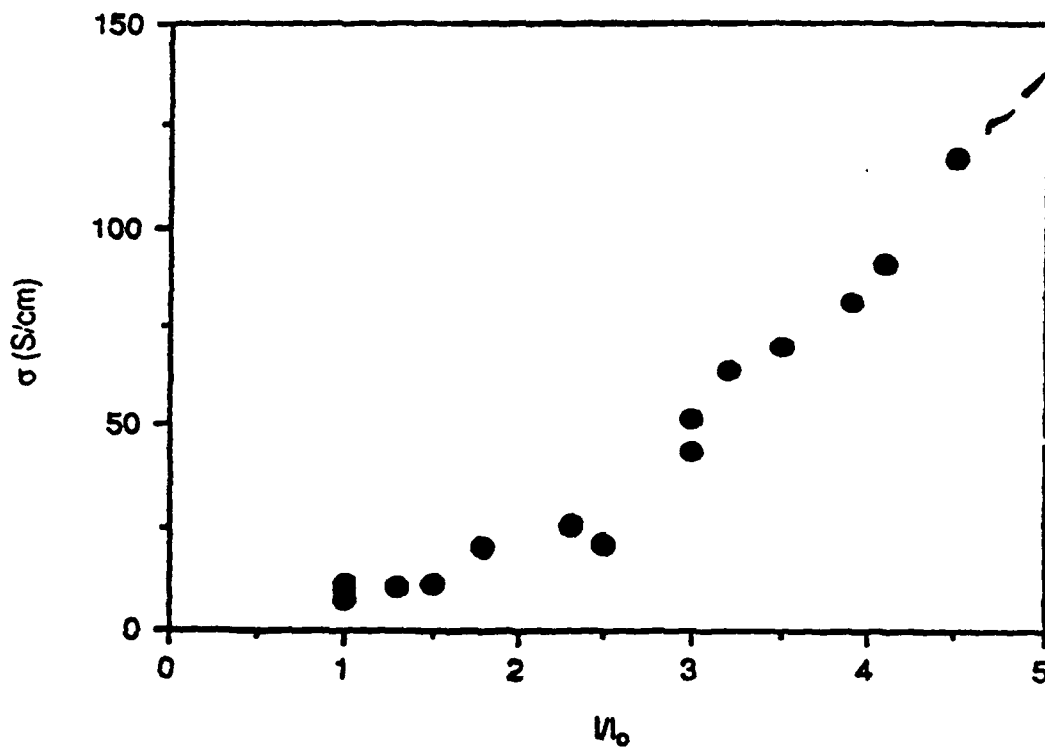
X-RAY DIFFRACTION OF EMERALDINE HYDROCHLORIDE FIBER



- STRESS—INDUCED INCREASE IN VOLUME % CRYSTALLINITY
- DUE PRIMARILY TO NUCLEATION OF NEW CRYSTALLITES —
NOT TO INCREASE IN SIZE OF ORIGINAL CRYSTALLITES (J. FISCHER)



Crystallinity vs. Draw Ratio (U_0) for Emeraldine.HCl Fibers
 [χ_c = fractional integrated radial intensity
 (sum of 010, 012, 200 crystal peaks)].



**Conductivity vs. Draw Ratio (l/l_0) for Emeraldine.HCl Fibers
(using low molecular weight polyaniline).**

MECHANICAL

PROPERTIES

TENSILE STRENGTH OF POLYANILINE FILMS (MPa) (EMERALDINE BASE)

FREE - STANDING FILM CAST FROM N. M. P. (15 wt% soln.)
(7 SAMPLES)
(GAUGE LENGTH = 3 INCHES)
(NON - STRETCHED)

BEST	59.9
AV.....	54.4

COMMERCIAL POLYMERS *

(NON - STRETCHED)

	<u>HIGH</u>	<u>LOW</u>
NYLON 66	83	77
NYLON 6	81	69
EPOXY (CAST RESINS)	90	28
POLYSTYRENE (GENERAL PURPOSE) ..	83	34
POLYMETHYL METHACRYLATE	76	48
(MOULDING GRADE)		

UNIAXIALLY STRETCHED (5 SAMPLES)

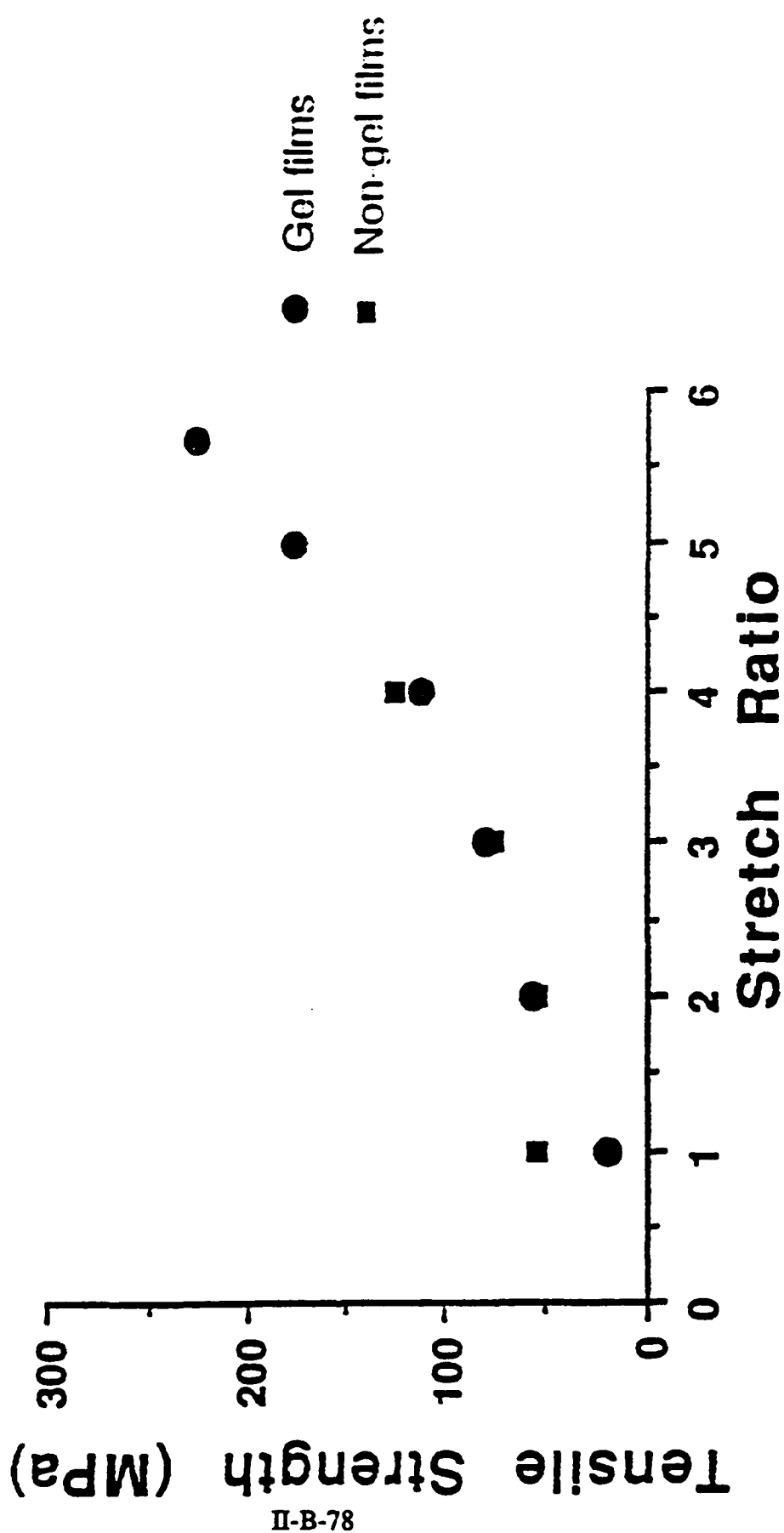
$l/l_0 = 4$

(STRETCHED)

BEST	144.8
AV.....	124.1

* POLYMER HANDBOOK

NOTE: TENSILE STRENGTHS OF FIBERS : = 3 TIMES
GREATER THAN THAT OF FILMS



MECHANICAL PROPERTIES **OF NYLONS**

TENSILE STRENGTH (MPa)

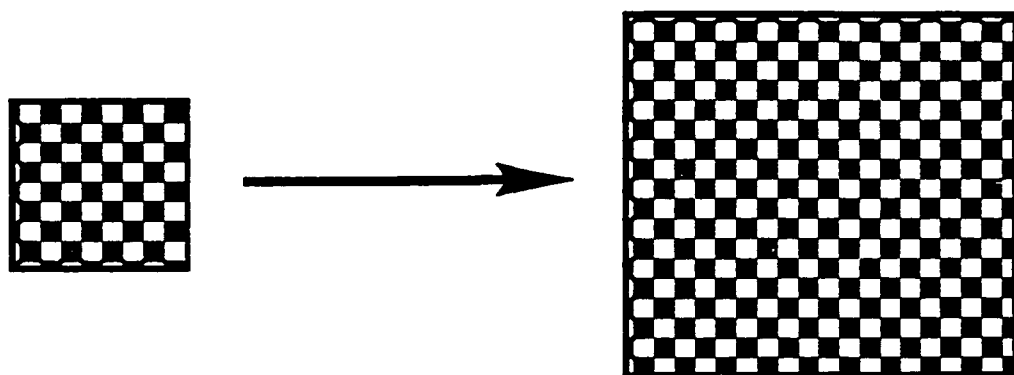
NYLON 6	80 (unoriented)
	475 - 550 (X4.3 oriented)
	675 - 775 (X5.0 oriented)

NYLON 66	90 (unoriented)
	575 - 600 (X4.3 oriented)
	650 - 875 (X5.0 oriented)

Reference: J. Brandrup and E. H. Immergut,
Polymer Handbook, 1975.

BIAXIALLY ORIENTED EMERALDINE BASE FILM

(≈15% N.M.P. PLASTICIZER ; T = 140°C ;
GAUGE LENGTH = 3 inches)



$$(l/l_0)_a = 2 \quad (l/l_0)_b = 2$$

TENSILE STRENGTH (MPa)

				<u>AV.</u>	<u>BEST</u>
EMERALDINE	BASE	(<u>B</u> iaxial)	($l/l_0 = 2$)	122.4	131.6
EMERALDINE	BASE	(<u>U</u> niaxial)	($l/l_0 = 2$)	53	62
NYLON 6		(<u>B</u> iaxial)		193-255*	

- POLYANILINE SHOWS SAME TYPE OF PROCESSIBILITY AS CONVENTIONAL POLYMERS

* ALLIED - SIGNAL PRODUCT DATA SHEET

MECHANICAL PROPERTIES OF POLYANILINE FIBERS

	<u>TENSILE</u> <u>STRENGTH</u> (M Pa)	<u>INITIAL</u> <u>MODULUS</u> (G Pa)
<u>EMERALDINE BASE</u>	366 (best)	8.6
STRETCH - ORIENTED (PARTLY CRYSTALLINE)	318 (av.)	8.1
<u>EMERALDINE.HCl</u>	176 (best)	5.0
(somewhat less crystalline)	150 (av.)	4.6

NOTE

<i>NYLON 6</i>	<i>200 - 905</i>
<i>NYLON 66</i>	<i>231 - 985</i>
<i>POLYESTERS</i>	<i>236 - 1,165</i>

ALL STUDIES ON 1 INCH GAUGE LENGTH.

SUMMARY

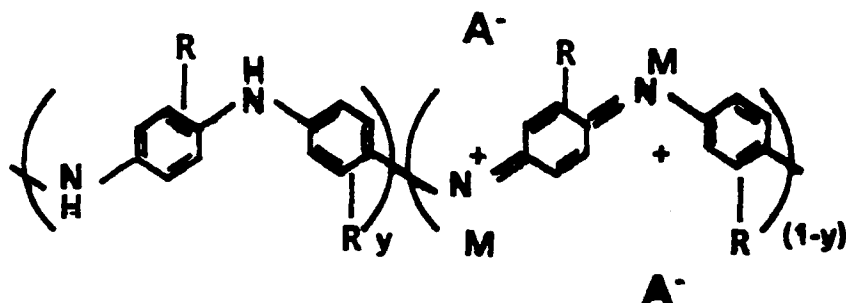
- THE MOLECULAR WEIGHT OF POLYANILINE CAN BE SIGNIFICANTLY INCREASED BY, e.g. REDUCING THE CONCENTRATION OF ANILINE SPECIES IN SOLUTION DURING ITS SYNTHESIS.
- CHAIN ENTANGLED POLYANILINE/POLYVINYLSULFONATE BEHAVES AS A SELF-DOPED SYSTEM.
- THE CONDUCTIVITY OF POLYANILINE IS GREATLY INCREASED BY THE PRESENCE OF NEUTRAL SALTS IN THE DOPANT ACID (DONNAN EQUILIBRIUM EFFECTS).
- THE CONDUCTIVITY OF POLYANILINE IS MORE (DIRECTLY) DEPENDENT ON ITS DEGREE OF ORIENTATION THAN ON ITS MOLECULAR WEIGHT.
- THE TENSILE STRENGTH OF POLYANILINE OVERLAPS THAT OF COMMERCIAL FIBERS/FILMS SUCH AS THE NYLONS, ETC.
- THE THERMAL STABILITY OF DOPED POLYANILINE CAN BE GREATLY INCREASED BY APPROPRIATE CHOICE OF DOPANT ACID.

FUTURE RESEARCH PLANS

- **USE ZONE-DRAWING TECHNIQUES UTILIZING CONVENTIONAL AND ALSO NETWORK HIGH MOLECULAR WEIGHT POLYANILINE FILMS IN ORDER TO INCREASE DRAW RATIO IN ORDER TO INCREASE :**
 - **CRYSTALLINITY**
 - **CONDUCTIVITY**
 - **TENSILE STRENGTH**
- **USE SHEARING TECHNIQUES TO INCREASE CRYSTALLINITY AND CONDUCTIVITY OF POLYANILINE POWDER.**
- **INVESTIGATE NEW (INORGANIC) DOPANTS FOR POLYANILINE AND THEIR THERMAL STABILITY FOR USE IN MICROWAVE WELDING STUDIES.**
- **REFINE SYNTHETIC METHODS FOR FURTHER INCREASING THE MOLECULAR WEIGHT OF POLYANILINE AND ITS BLOCK CO-POLYMERS.**

PHYSICAL PROPERTIES,
STRUCTURE
AND
ELECTRONIC CONCEPTS
OF
POLYANILINE

THE POLYANILINES



Vary oxidation state:

$(1-y) = 0$ Leucoemeraldine

$(1-y) = 0.5$ Emeraldine

$(1-y) = 1.0$ Pernigraniline

(Pseudo) protonic acid dope or oxidize / reduce:

$M^+ = H^+, CH_3^+, \text{tosylate}, \dots$

$A^- = Cl^-, PF_6^-, CH_3SO_4^-, \dots$

Derivatize:

$R = -CH_3, -OCH_3, SO_3^-, \dots$

Control: Molecular weight

Crystal structure

% Crystallinity / orientation

Amorphous order / orientation

blending

.

.

.

POLYANILINES:

PHYSICAL PROPERTIES / ELECTRONIC CONCEPTS

1986 - Pre-URI:

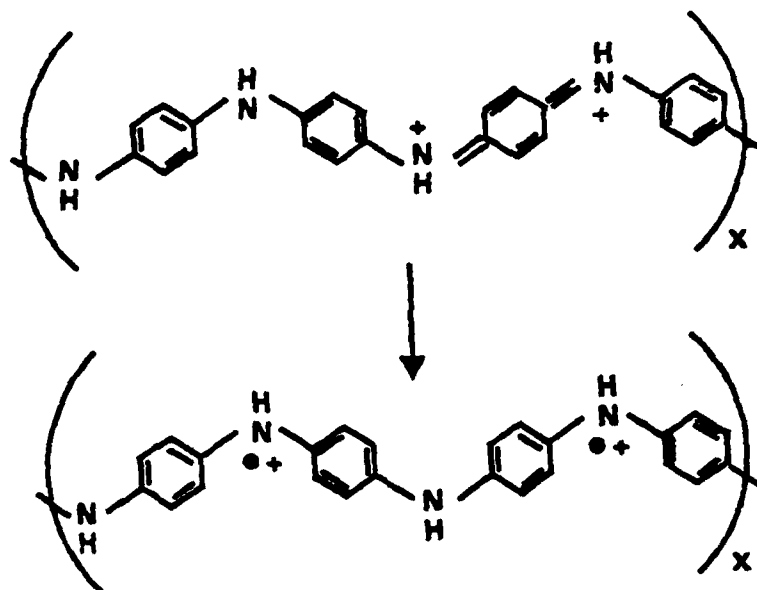
- Early physical studies of conductivity, thermopower, UV-Vis absorption and EPR of poorly characterized samples lead to suggestion of only localized charges or formation of diamagnetic bipolarons in protonated materials
- Lack of reproducibility due to uncertainties in composition, oxidation state, etc., caused much confusion on those properties measured
- Concepts used were either localized chemical pictures or borrowed from polyacetylene terminology

POLYANILINES:

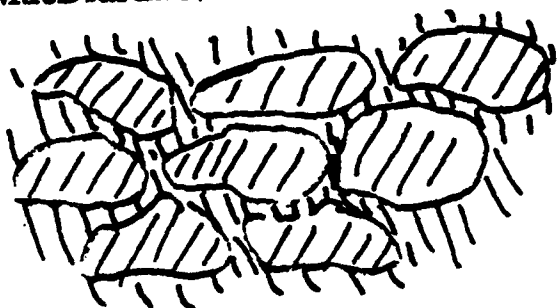
PHYSICAL STUDIES / ELECTRONIC CONCEPTS

1986-87:

- Proposed and demonstrated poly-(semiquinone) or polaron lattice was formed in emeraldine upon protonation (magnetic susceptibility / spectroscopy) (Epstein / MacDiarmid)



- Proposed and demonstrated that upon protonation, emeraldine formed a granular metal dominated by charging energy limited tunneling [$\sigma(T)$, $\sigma(E)$, $S(T)$] $\sigma \sim 1S/cm$ (Epstein / MacDiarmid)



II-B-87

- Proposed exciton (2 eV) dominated optical spectrum of emeraldine base (spectroscopy) (Epstein / MacDiarmid)
- Demonstrated effect of moisture primarily is on barriers between islands [σ (10^1 - 10^{10} Hz)] (Epstein / MacDiarmid)
- Study of tetramer model systems (with Allied Signal Corp.) showed that bipolarons form on confinement (Epstein)
- Initial photoinduced spectroscopy proved exciton assignment (Epstein / MacDiarmid)
- Measured extremely large controllable microwave absorption of doped emeraldine (Epstein / MacDiarmid)
- Electrochemistry as a function of pH and potential revealed a four-part phase diagram for polyaniline (Yang)

1988-89:

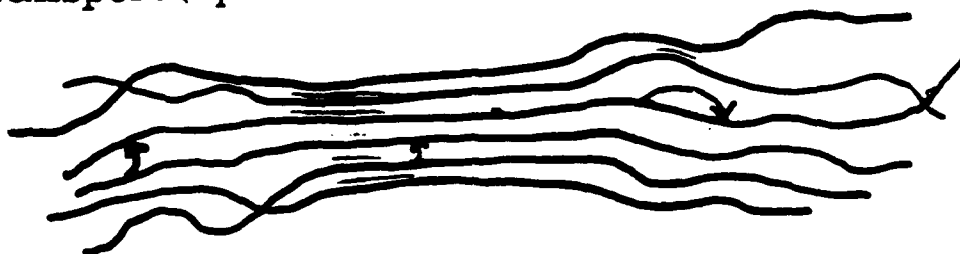
- First determination of crystal structure of emeraldine base (Epstein / MacDiarmid)
- First discovery of two different crystal structures for metallic emeraldine salt, ES-I and ES-II (Epstein / MacDiarmid)
- First discovery of nonmetallic doped amorphous phase of emeraldine salt, ES-II' (Epstein / MacDiarmid)
- First determination that polarons in polyaniline differ dramatically from those of polyacetylene and other earlier studied polymers - new physics (Epstein)
- First proposal for new model for massive polarons in large gap polymers (Epstein)
- First proposal of central role of ring conformations (Epstein)
- First measurement of unusually short (10^{-12} s) and long (10^4 s) time dynamics for excitations in polyaniline (Epstein / MacDiarmid)
- First report of large nonlinear optical response in polyaniline ($\chi^{(3)} \sim 10^{-8}$ esu) (Epstein / MacDiarmid)

- First spectroscopic study of metallic polymer states in solution (MacDiarmid / Epstein)
- First photoinduced spectroscopic study of metallic polymer states in solution, role of interchain excitation (Epstein / MacDiarmid)
- First measurement of and new model for charge conduction in insulating polyaniline (Epstein / MacDiarmid)
- First published microwave frequency ϵ and σ yielded new models for unusual absorption - predict true metallic behavior ($> > 250 \text{ S/cm}$) (Epstein / MacDiarmid)
- First detailed composition and temperature dependent electron spin resonance confirmed insulator-to-metal transition (Epstein / MacDiarmid)
- First proposal of new concept of "textured" metallic islands to reflect role of spatial variation of local order (Epstein / MacDiarmid)
- First control of polaron / bipolaron equilibrium through breaking of translational symmetry (MacDiarmid / Epstein)

- First measurement of anisotropic optical and transport properties of oriented films (Epstein / MacDiarmid)

1989-90:

- Detailed general model for electronic structure and charge defects of ring-containing polymers such as polyaniline and PPS, which accounts for thermochromism and photo- and doping-induced charge defects (Epstein)
- Determination of effects of derivatization and oxidation on crystal structure (Epstein / MacDiarmid)
- Determination through x-ray and IR of orientation in aligned polyaniline (Epstein / MacDiarmid)
- Controlled charge conduction (dc through microwave) in polyaniline derivatives (PAN, POT, and SPAN) - interchain versus intrachain charge transport (Epstein / MacDiarmid)



- Photoinduced spectroscopy and ESR confirm massive polaron and soliton nature of charge states in pernigraniline and other polyaniline oxidation states and derivatives (Epstein / MacDiarmid)
- Determination of polaron nature of 0.9 eV absorption through electrochemical study (Yang)
- Determination of short time response (10^{-13} s - 10^{-9} s) of C₆ rings due to motion of charge (Epstein / MacDiarmid)
- Control of the long time response to light with oxidation state / derivatization - stabilization of erasable optical information storage to 250 K (Epstein / MacDiarmid)

SUMMARY

POLYANILINE: PHYSICAL STUDIES / ELECTRONIC CONCEPTS

<u>Pre-URI</u>	<u>1987</u>	<u>1988</u>	<u>1989-90</u>
<u>Electronic Structure</u> Diamagnetic resonance forms	Paramagnetic polaron lattice / polysemiquinone, excitons	Massive polaron; role of ring conformation; novel long-time dynamics and short-time dynamics; base and two salt crystal structures; "textured" metallic islands; localization in solution; polarization of optical phenomena; NLO; generalization from EB and ES to LB, PN, PPS, PPO, and other ring containing polymers	Electronic and polaron structure; thermochromism; determination of orientation and crystal structure in aligned films; controlled response of derivatives: short time (ps) and long time (optical information storage); role of amorphous versus crystalline regions
<u>Charge Transport</u> Hopping conduction	Charging energy limited tunneling in granular polymeric metal Effects of moisture primarily of barriers	100 fold increase in σ in oriented films and in fibers, barrier remains; loss tangent control through derivatives	Enhanced conductivity of oriented films and fibers; controlled response of derivatives (dc conductivity through microwave loss); role of interchain and intrachain transport; amorphous versus crystalline regions

1990-91:

- Determination of origin of high conductivity/microwave loss in polyanilines: 3-D charge delocalization in ordered regions.
- Microwave conductivity of polyaniline/host composites – gaskets for strong welds
- Conductivity, thermopower, and structure of poly(ethoxyaniline): role of chain entanglement
- Use Kramers-Kronig analysis of reflectance and transmission of oriented emeraldine salt films to determine that ultimate conductivity (if higher order achieved) is $> 10^3$ S/cm.
- Determine crystal structure for pernigraniline and leucoemeraldine oxidation states
- Determine crystal structure and its evolution with doping for methyl derivative, poly(o-toluidine)
- Determine evolution of amorphous local order with doping and dedoping – structural origin of memory effect
- Determination of evolution of photoinduced polaron mass with C₆ ring substituent (methyl, ethyl, propyl) in emeraldine and pernigraniline base

- Discovery of unusual independence of ring and bond order parameters in Peierls ground state of pernigraniline base
- Discovery via photoinduced absorption and light-induced electron spin resonance of independent short-lived, light-mass solitons and long-lived, heavy-mass ring-torsion-angle polarons in pernigraniline base
- Proposal of lower effective mass solitons in leucoemeraldine base through 90° ring rotations
- Determination of growth dynamics of long-lived photoinduced defects using photoinduced absorption and light-induced electron spin resonance in emeraldine base and pernigraniline base: formation of polaron droplets
- Determination of picosecond time dynamics of luminescence of leucoemeraldine base in NMP solution: role of intra-ring exciton
- Extend long-lived photoinduced studies of EB and PNB to ultraviolet: discover new long-lived peak
- Picosecond photoinduced absorption studies of solutions of EB: essential role of C_6 torsion dynamics
- Determine ability of sulfonic acid derivitized polyaniline to electronically modulate pH and enzyme activity of surrounding medium

**POLYANILINE:
ON THE EDGE
OF
3-D DELOCALIZATION**

II-B-96

Figure 1: X-ray Diffraction of Emeraldine Hydrochloride Fiber

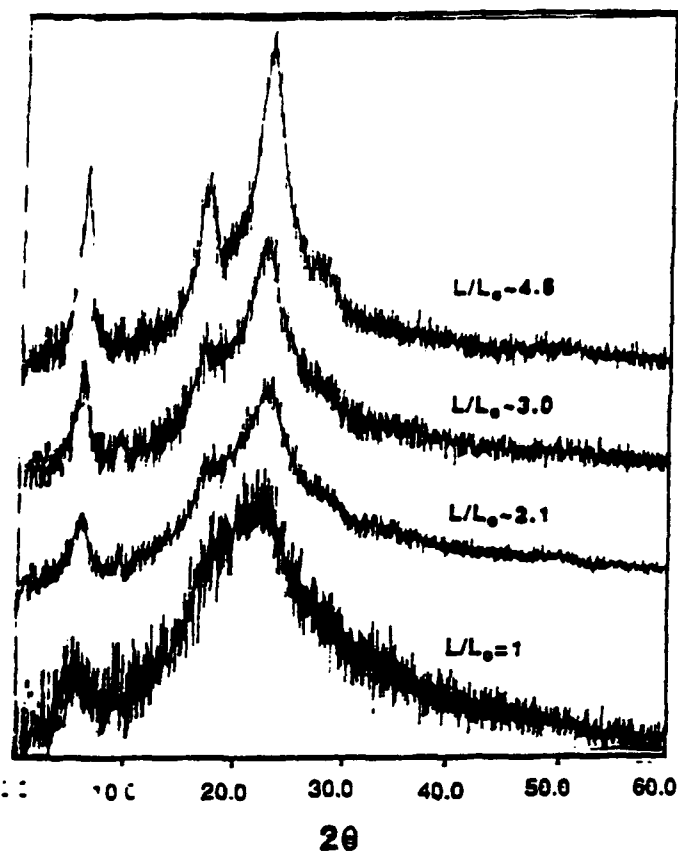


Figure 2: Draw Ratio vs. Estimated Degree of Crystallinity of Emeraldine Hydrochloride Fibers

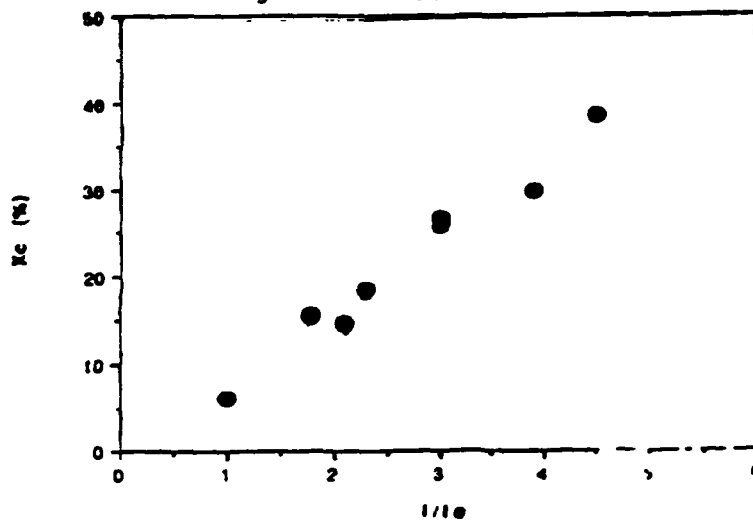


Figure 3: Estimated Degree of Crystallinity vs. Conductivity of Emeraldine Hydrochloride Fibers

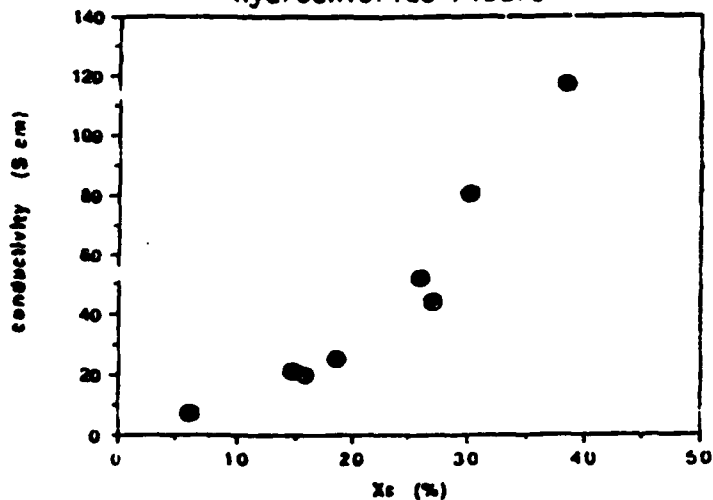
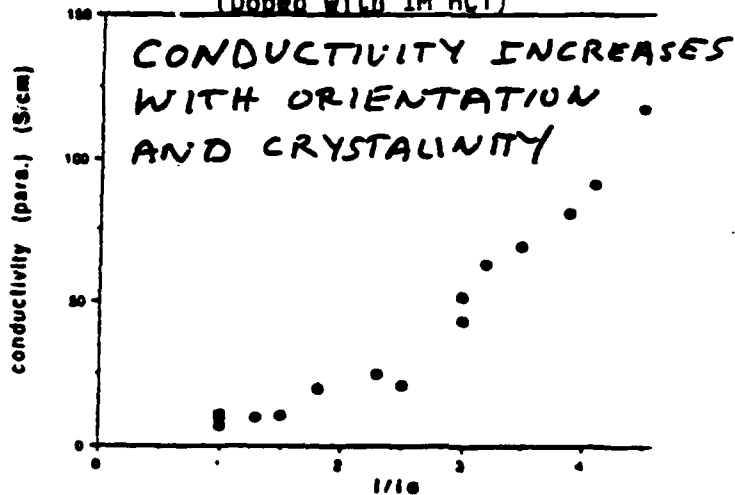


Figure 4: Conductivity (parallel) vs. L/L_0 of Polyaniline (Emeraldine Base) Fibers (Doped with 1M HCl)

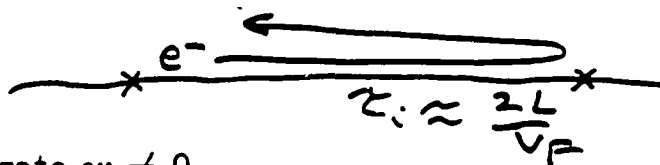


1) Draw fiber (in water) from emeraldine base solution in NMP (pre-formed fiber) at -120°C (RS) for -15 min.
 2) Draw fiber at -140°C (RS)
 (all fibers from same batch of pre-formed fiber)

CONDUCTIVITY IN QUASI-1-DIMENSION

- Electron states are localized in strictly 1d disorder system with any weak disorder

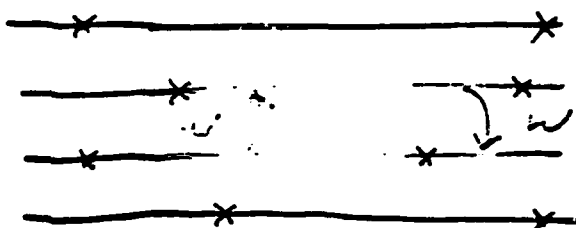
see PHILLIPS



- Q1d-DS: interchain diffusion rate $w \neq 0$.

◦ $w > w_c$: Metallic states

◦ $w < w_c$: Localized states



- For $w < w_c$, localization length increases with w .

$$w \sim \frac{\hbar}{4\tau_L}$$

- w increases with

◦ interchain transfer integral t_\perp

◦ interchain coherence ξ

◦ intrachain mean free time τ_i

FOR 3-d DELOCALIZATION

$$w \gtrsim \frac{\hbar}{\tau_i}$$

- For low T and $w \ll w_c$, Q1d-VRH

◦ Interchain hopping:

$$\ln \sigma \propto -(T_0/T)^{1/2} \quad S(T) = \text{const.}$$

$$T_0 = \frac{2\pi\hbar^2}{k_B} \frac{1}{N(E_F)^2}$$

◦ Intrachain hopping:

$$\ln \sigma \propto -(T_0/T) \quad S(T) \propto 1/T$$

FIRSOV
et al.

- Metal islands ($w > w_c$ and barriers)

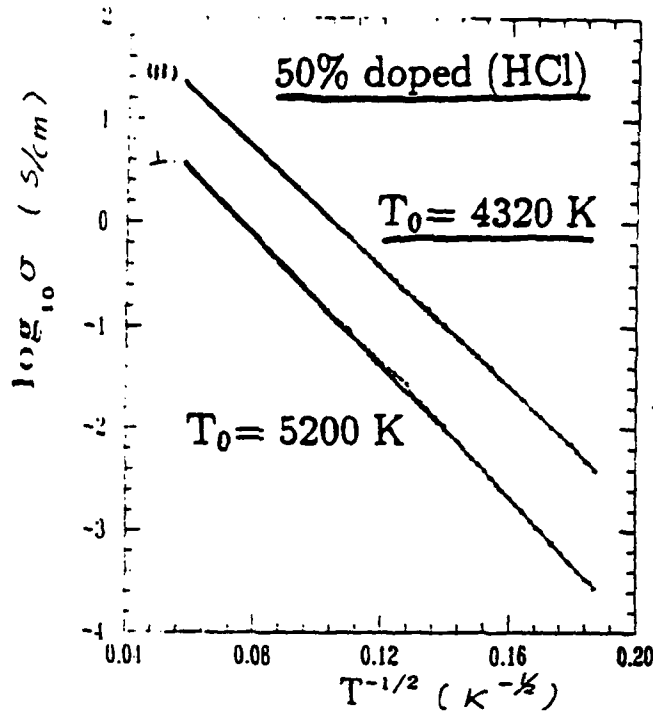
◦ Sheng model:

$$\ln \sigma \propto -(T_0/T)^{1/2} \quad S(T) \propto T$$

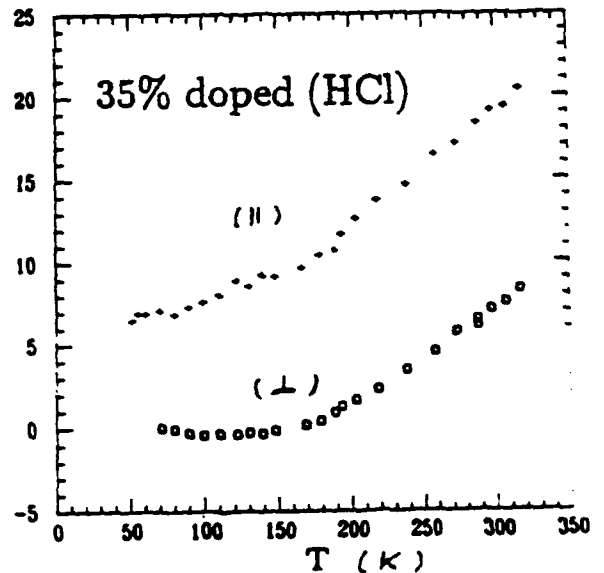
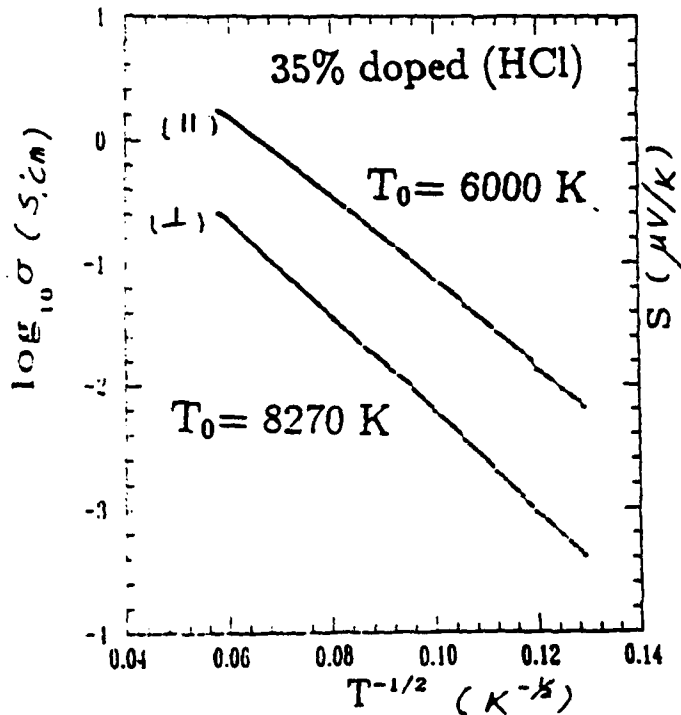
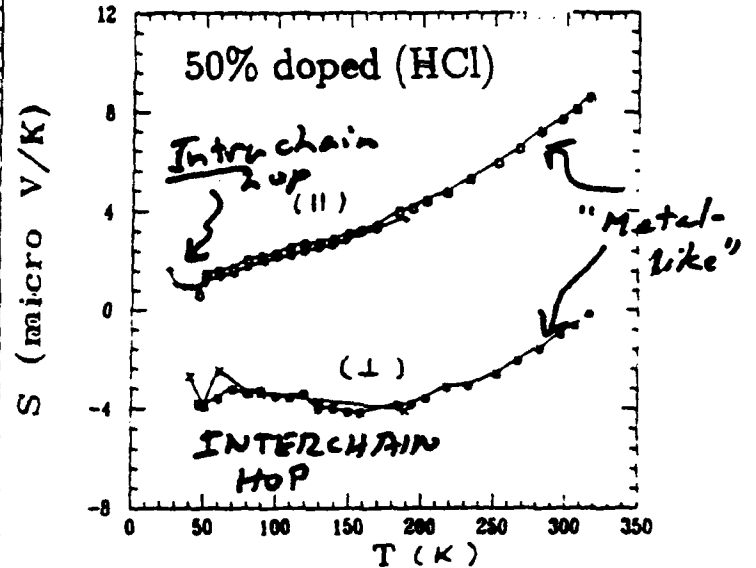


1:4 Stretched PAN Film

DC Conductivity



Thermopower



$$\ln \sigma \propto - \left(\frac{T_0}{T} \right)^{1/2}$$

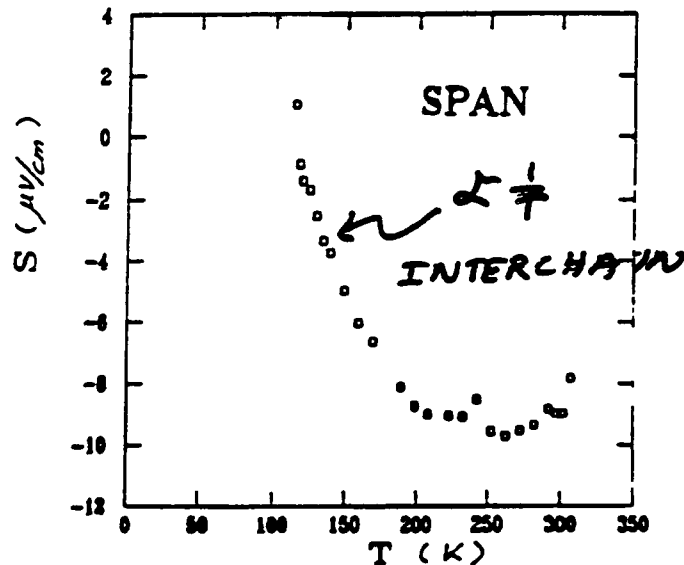
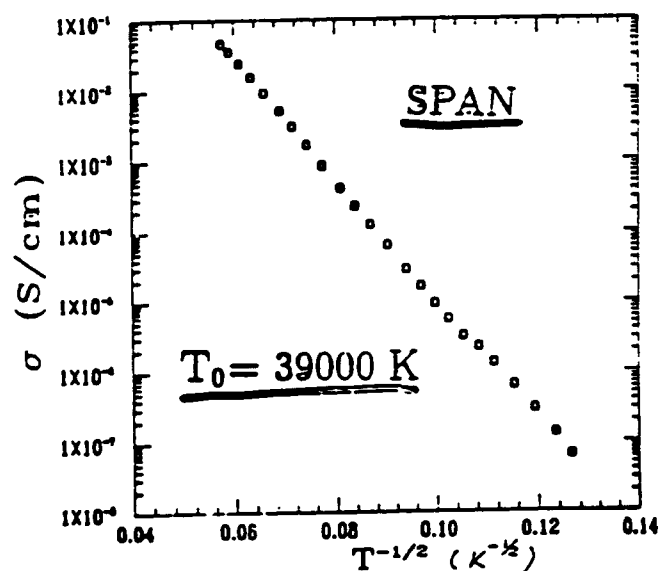
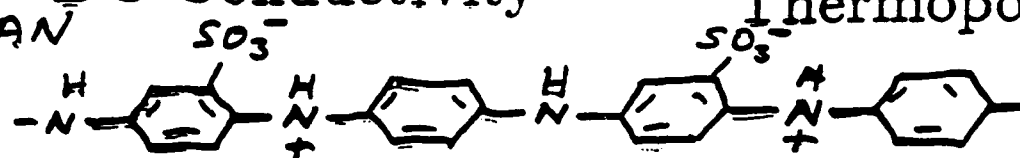
II-B-99

Quasi-1-d VRH
+ TUNNELING

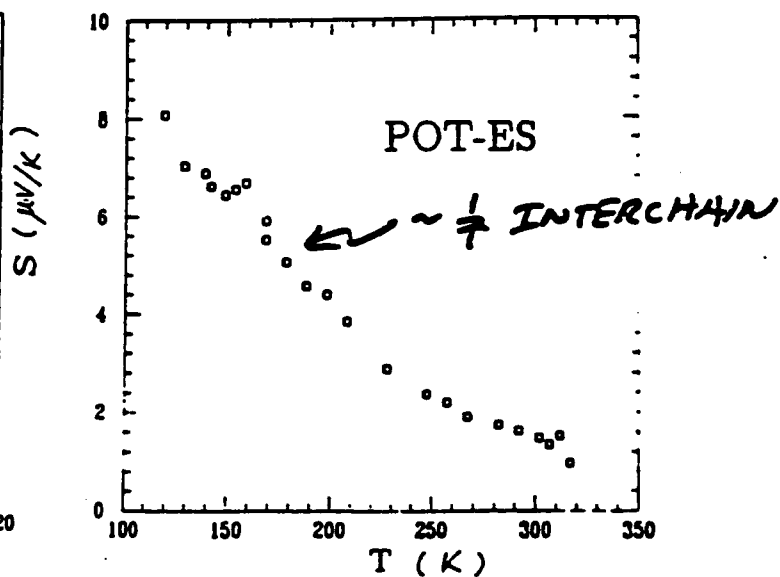
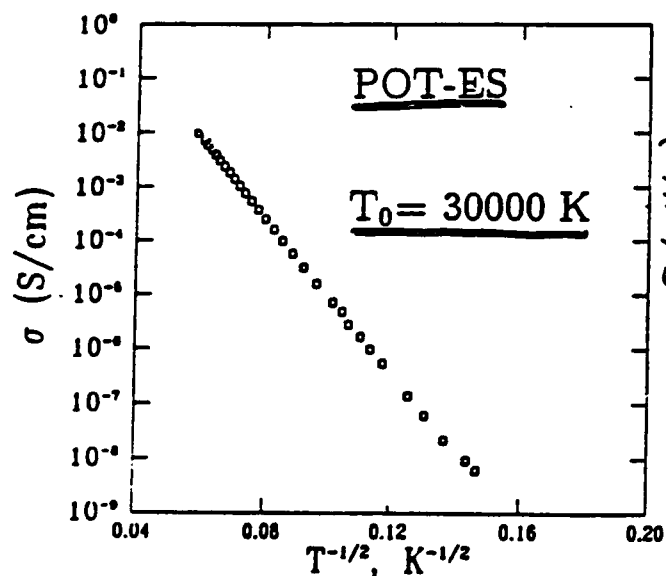
DC Conductivity

Thermopower

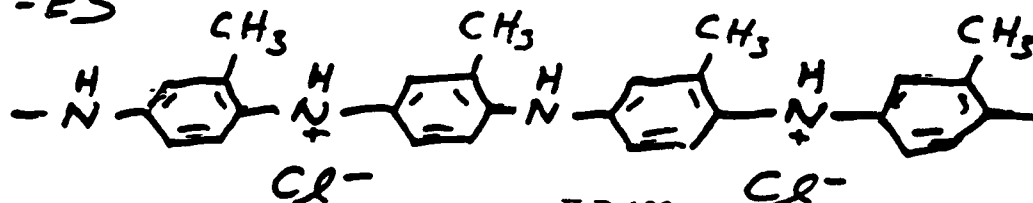
SPAN



QUASI-1-D VRH

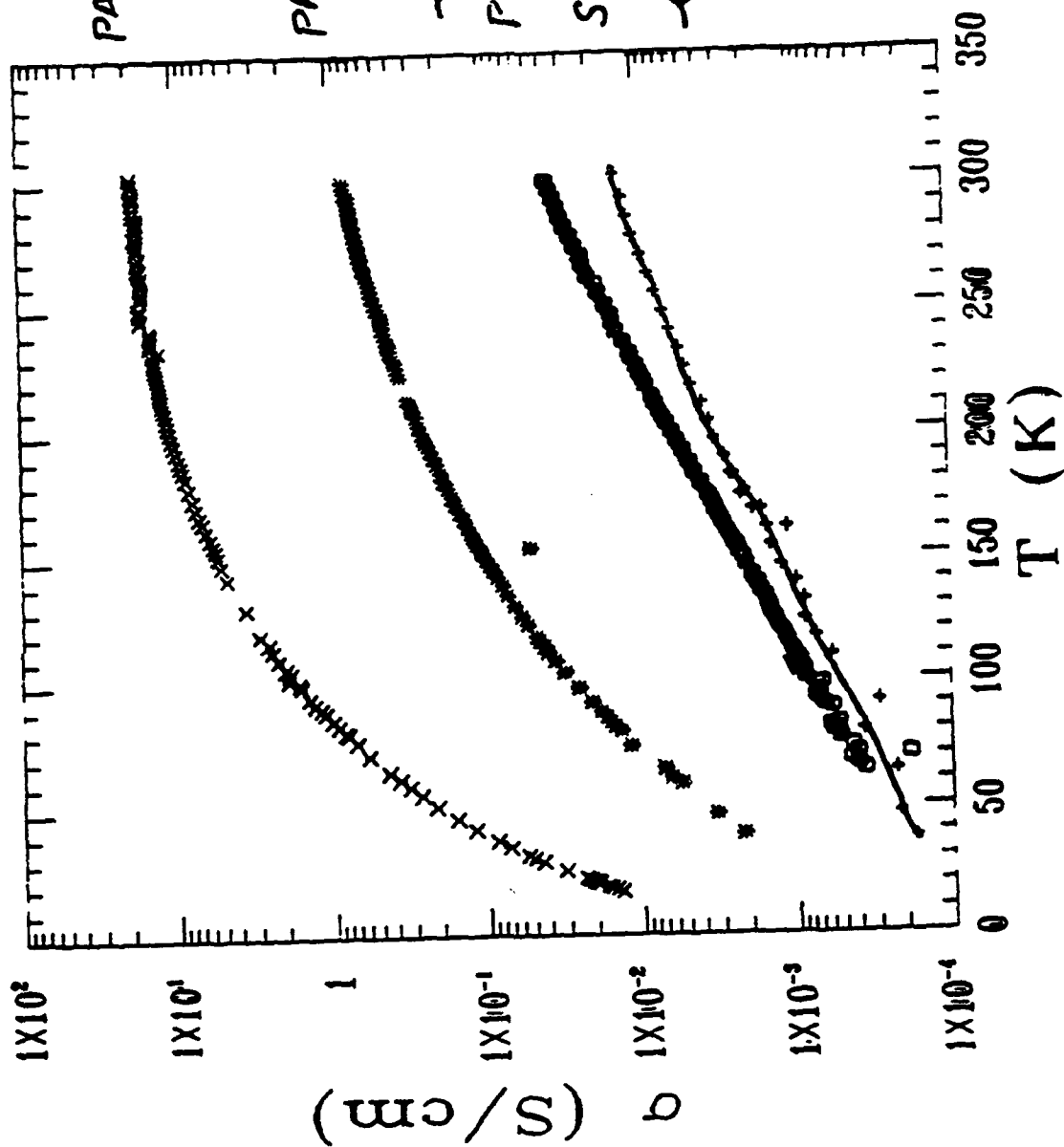


POT-ES

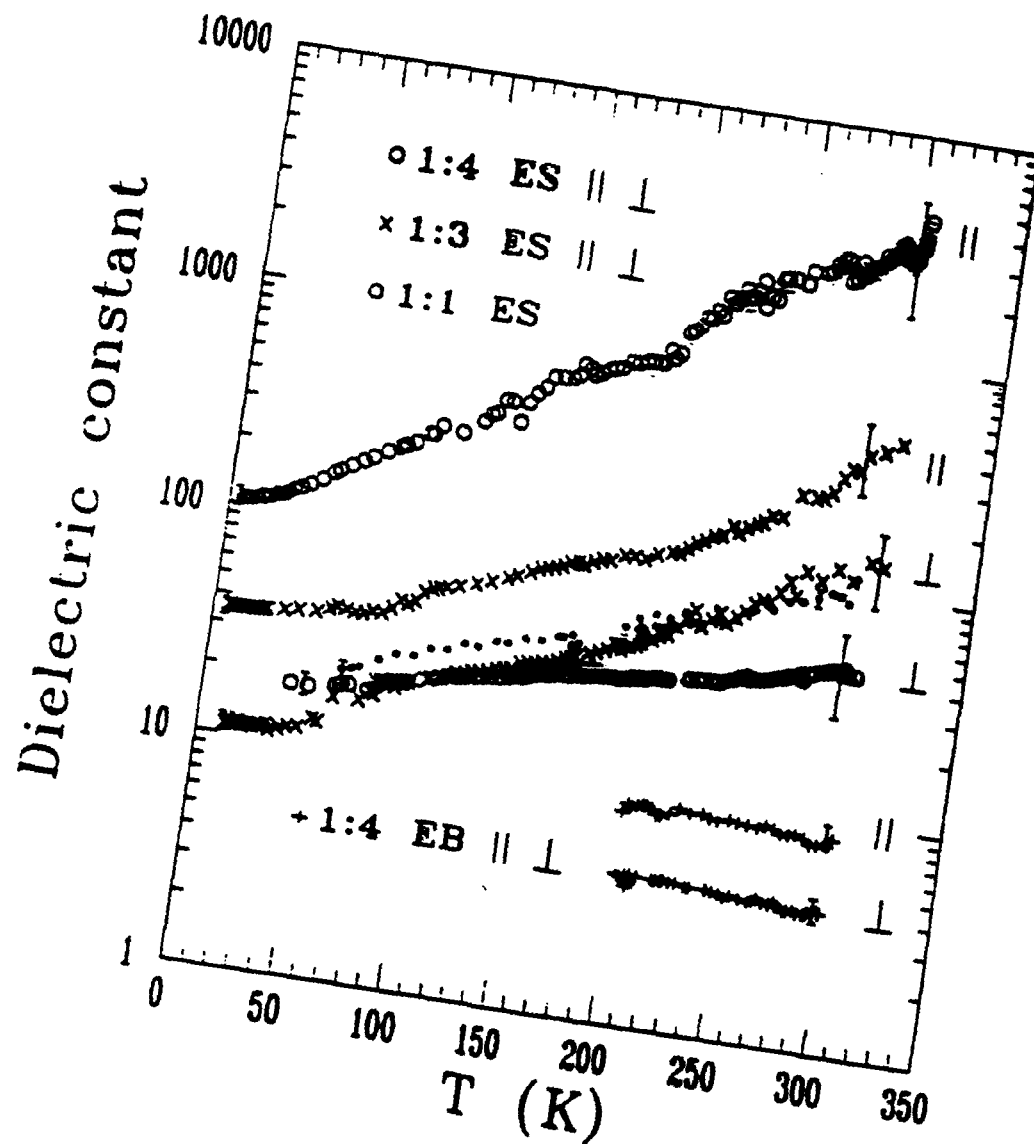


II-B-100

6.5 x 10⁹ Hz, PUMPED SAMPLES

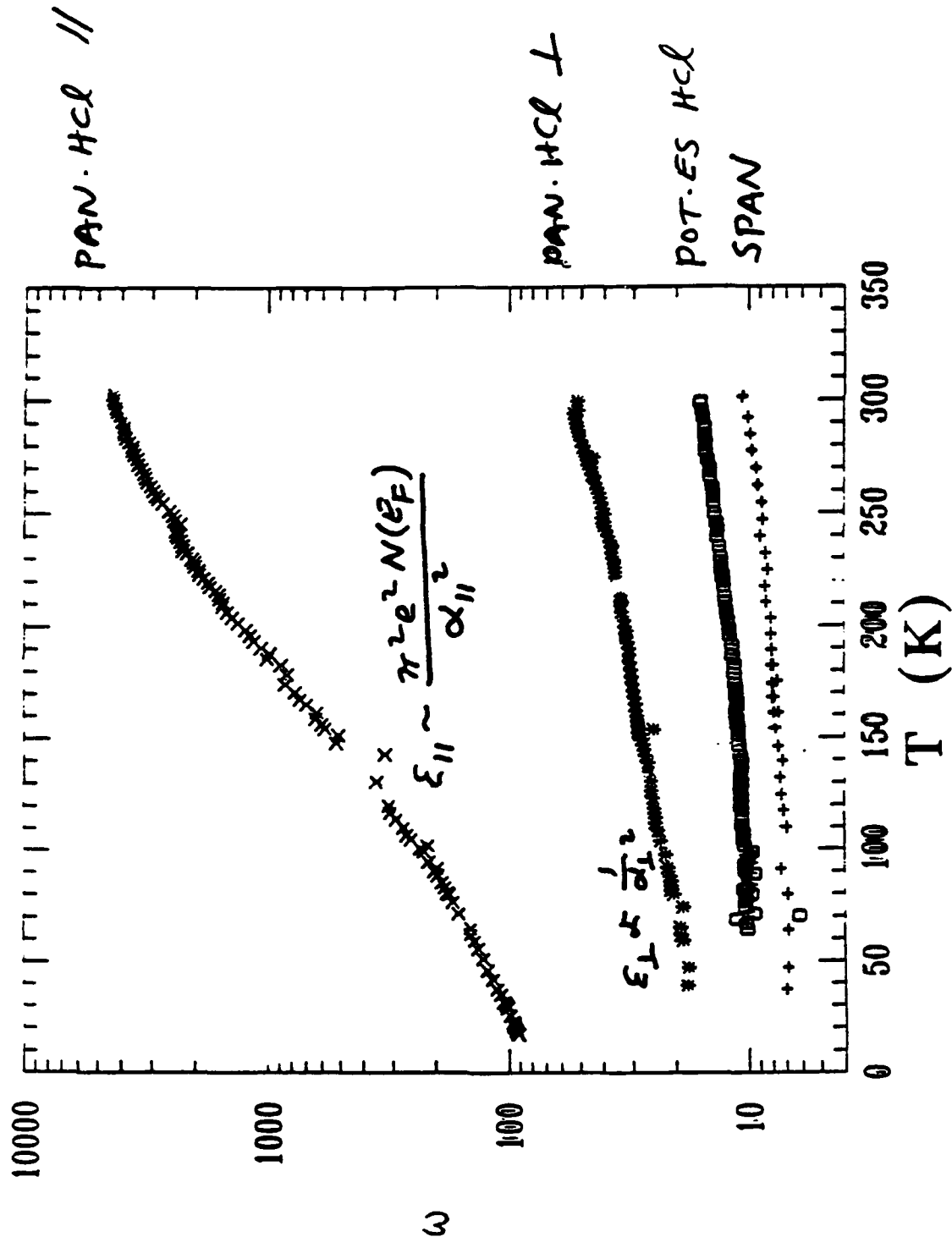


EMERALDINE SALT
6.5 GHz DIELECTRIC CONSTANT
VS ORIENTATION

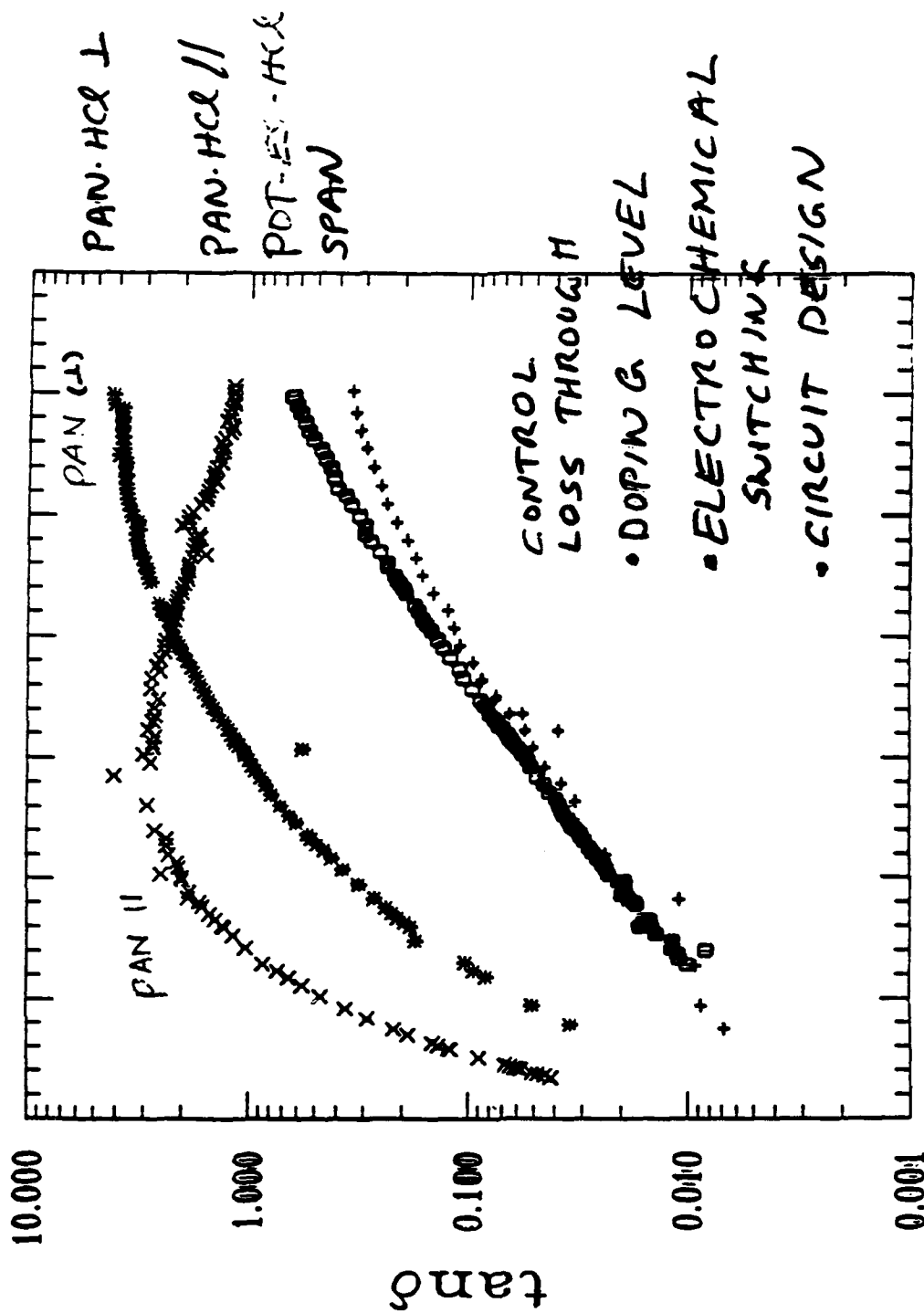


$$\epsilon \sim \frac{\pi^2 e^2 N(E_F)}{\alpha^2} [LOW T]$$

$6.5 \times 10^9 \text{ Hz}$



$6.5 \times 10^9 \text{ Hz}$



COMPARE TO LOSS OF $\tan \delta \sim 0.1 - 1$ FOR
COMMERCIAL MATERIALS

Dielectric Constant

For a rectangular box of L_1, L_2, L_3

$$\epsilon \approx \epsilon_{\infty} + (2^{9/2}/\pi^3) e^2 N(E_F) L_i^2 \quad (10)$$

At $T \rightarrow 0$ K,

For PAN-ES, $\epsilon = 30 \Rightarrow L \sim 20 \text{ \AA}$

For POT-ES, $\epsilon = 7 \Rightarrow L \sim 6 \text{ \AA}$

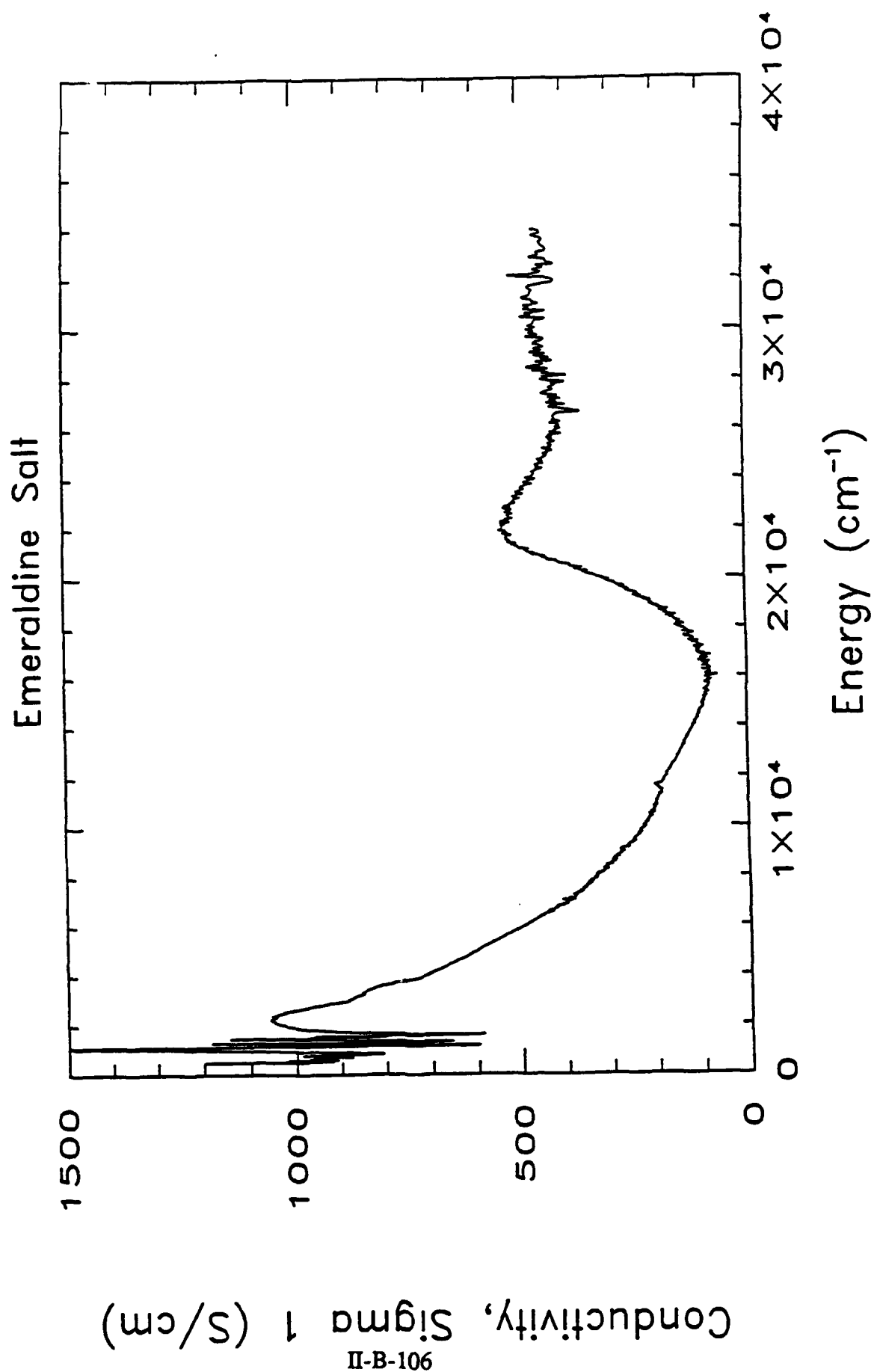
For SPAN, $\epsilon = 3.5 \Rightarrow L \sim 4 \text{ \AA}$

FOR ORIENTED (4:1) PAN-ES%

$$\epsilon_{||} = 100 \Rightarrow L \sim 40 \text{ \AA} \text{ (8 rings)}$$

$$\epsilon_{\perp} = 25 \Rightarrow L \sim 18 \text{ \AA} \text{ (~5 chains)}$$

DELOCALIZED (METALLIC) REGION
CORRESPONDS TO SIZE OF
CRYSTALLINE REGIONS



II-B-106

• PAN-ES:



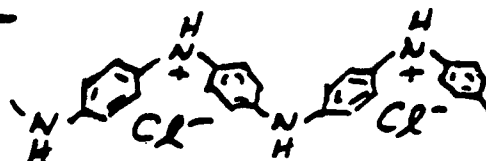
Parallel

◦ "Localization length" $> 50 \text{ \AA}$

◦ "Perpendicular" $> 20 \text{ \AA}$

◦ σ_{DC} : 3-d motion, barriers important.

◦ "Thouless localization" within crystalline regions



GIORH
HOPPING/TUNNELING

• POT-ES: more localized than PAN-ES.

◦ Localization length $\sim 8 \text{ \AA}$

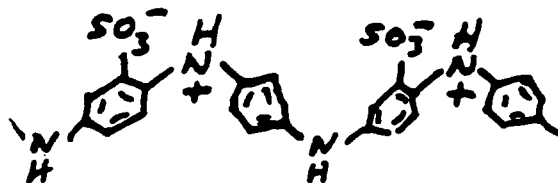
◦ σ_{DC} : Quasi-1d-VRH



• SPAN-ES:

◦ Localization length $\sim 6 \text{ \AA}$

◦ σ_{DC} : Quasi-1d-VRH



• Localization is caused by decreased interchain diffusion rate

◦ increased interchain separation

◦ decreased interchain coherence

◦ decreased crystallinity

• Highly conductive "metallic" polymers require maximizing

interchain coherence, bandwidth and intrachain scattering time.

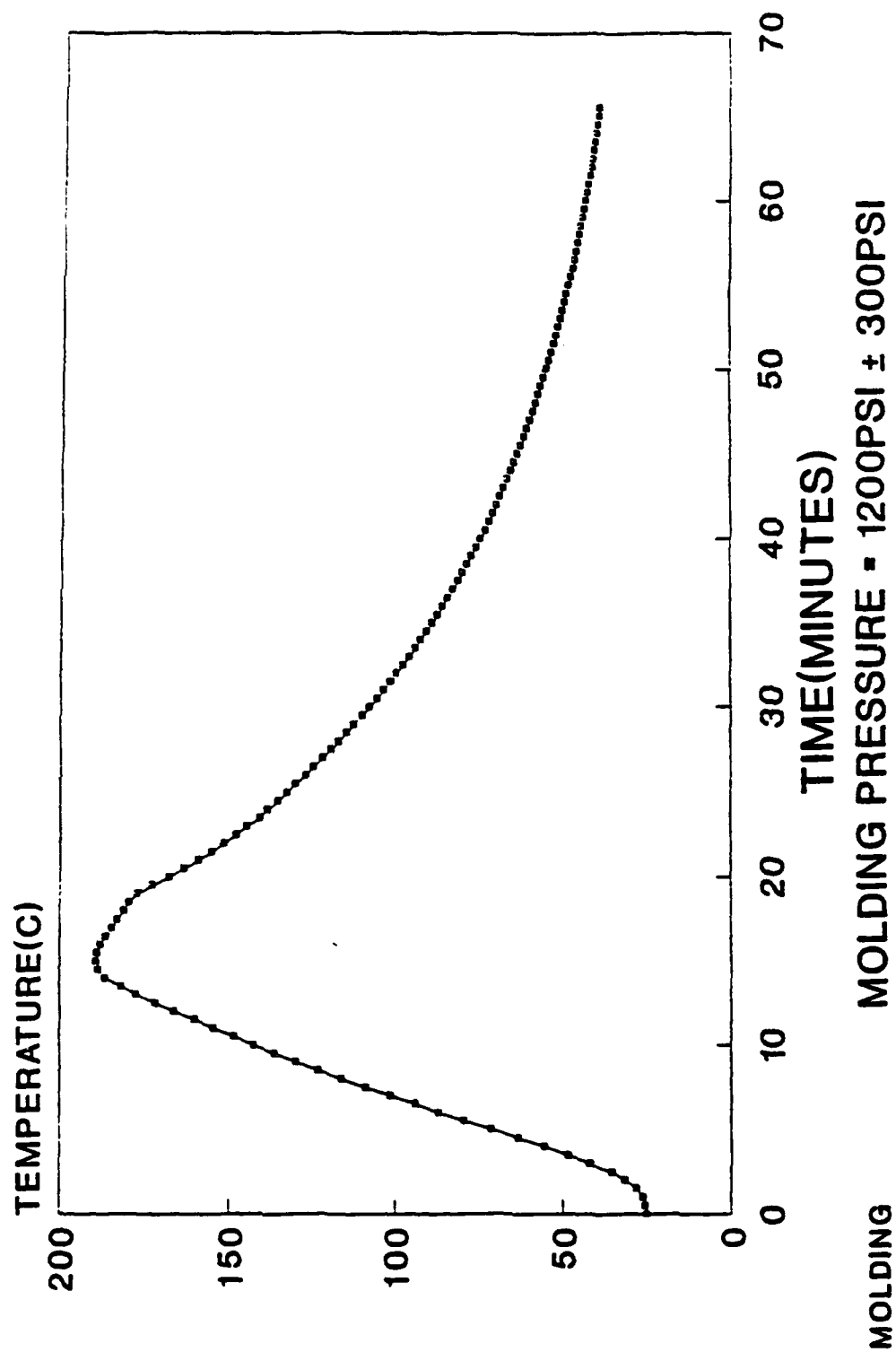
POLYANILINE IS ON EDGE OF
3-D DELOCALIZATION IN
CRYSTALLINE REGIONS

**POLYANILINE
FOR
STRONG MICROWAVE WELDS**

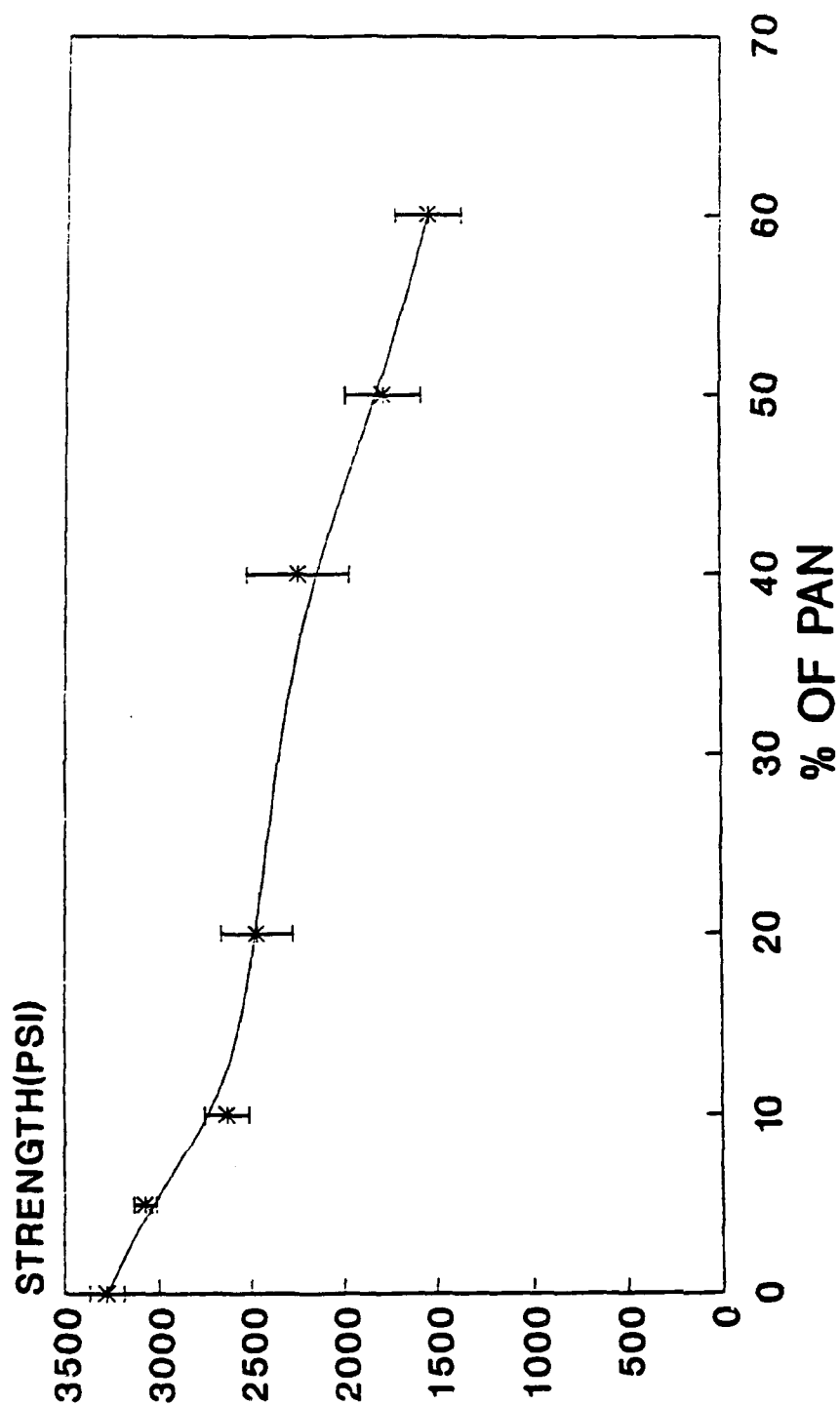
**In collaboration with A. Benatar, Department of Welding Engineering,
The Ohio State University**

II-B-108

COMPRESSION MOLDING POLYANILINE + HDPE



TENSILE TEST OF PAN COMPOSITE POLYANILINE + HDPE POWDER COMPRESSION MOLDING

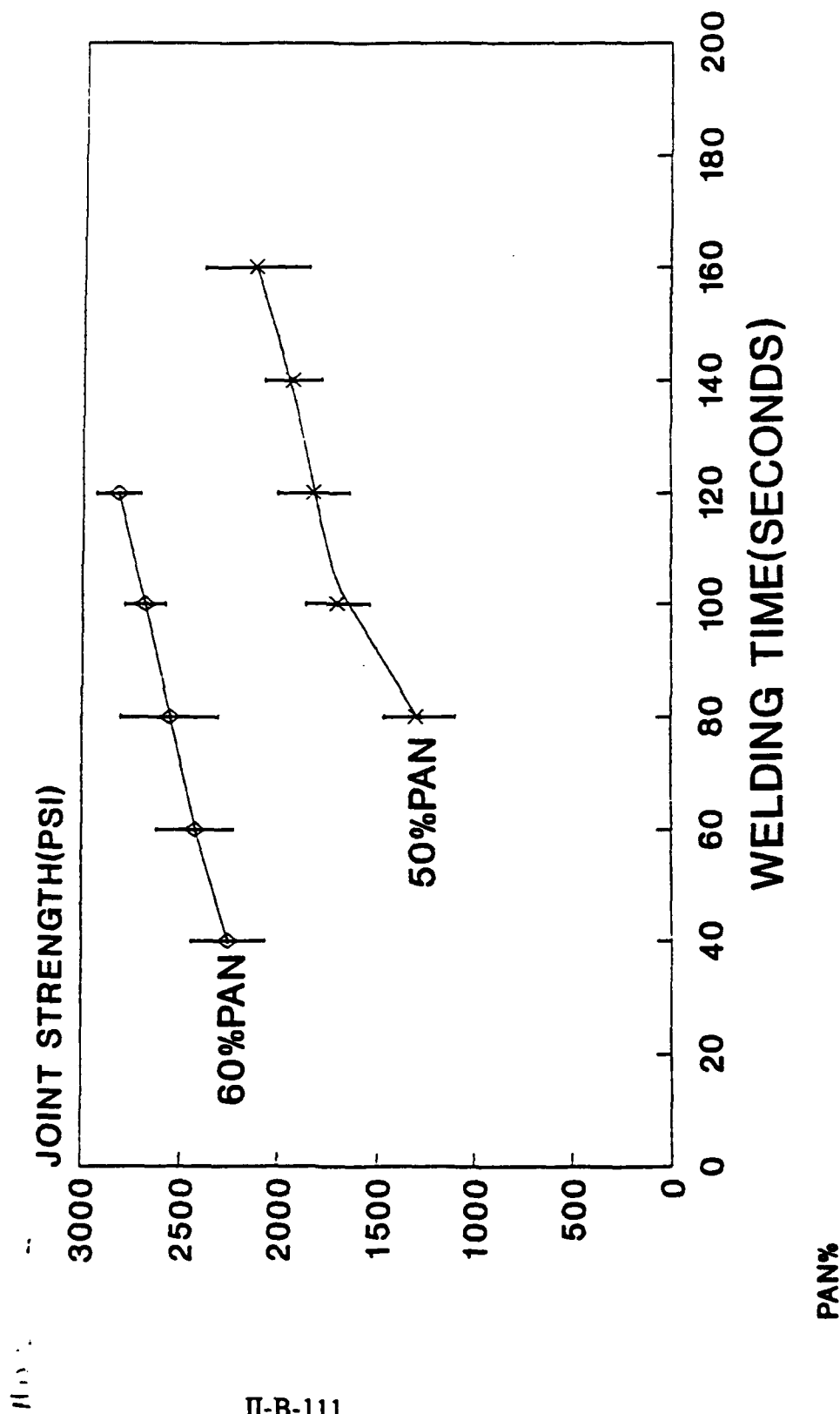


PANTEN

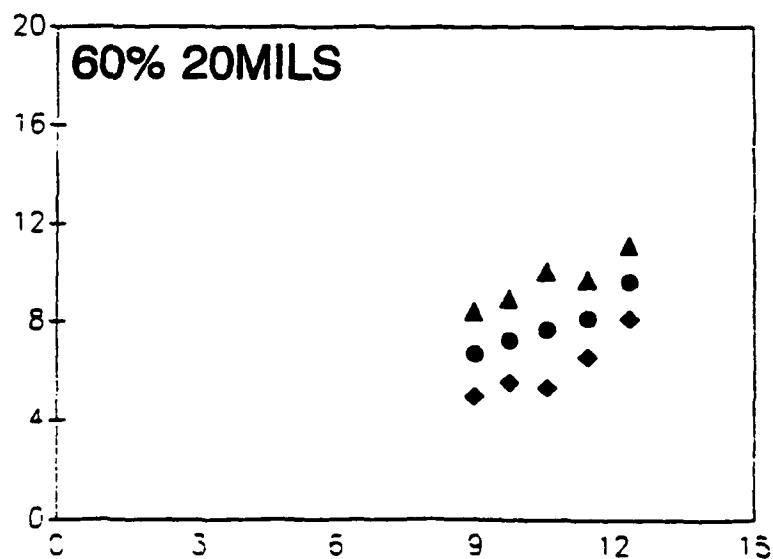
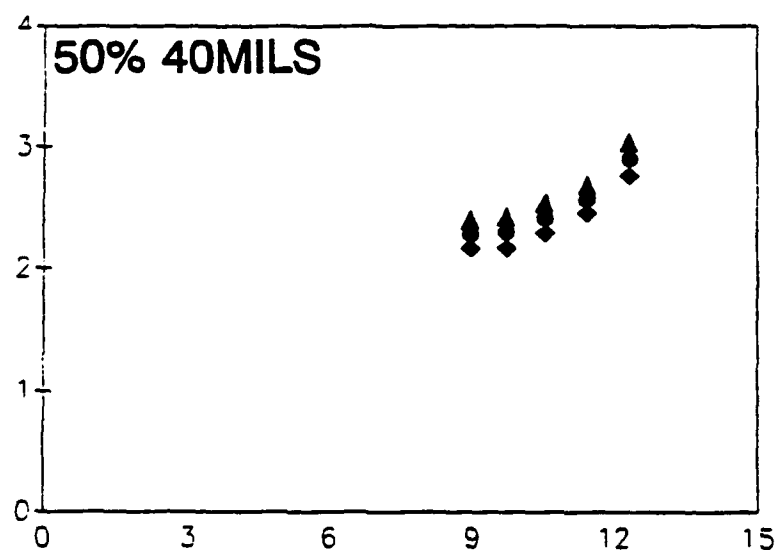
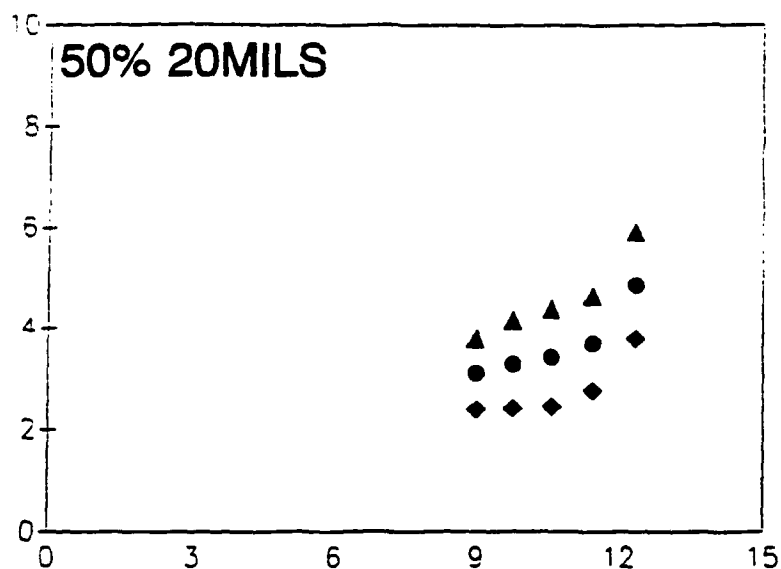
MICROWAVE WELDING HDPE

EFFECT OF %PAN

PRESSURE=43PSI THICKNESS=20MILS



Microwave Conductivity (S/Cm) (E-2)



8.976
9.741
10.654
11.432
12.335
GHz

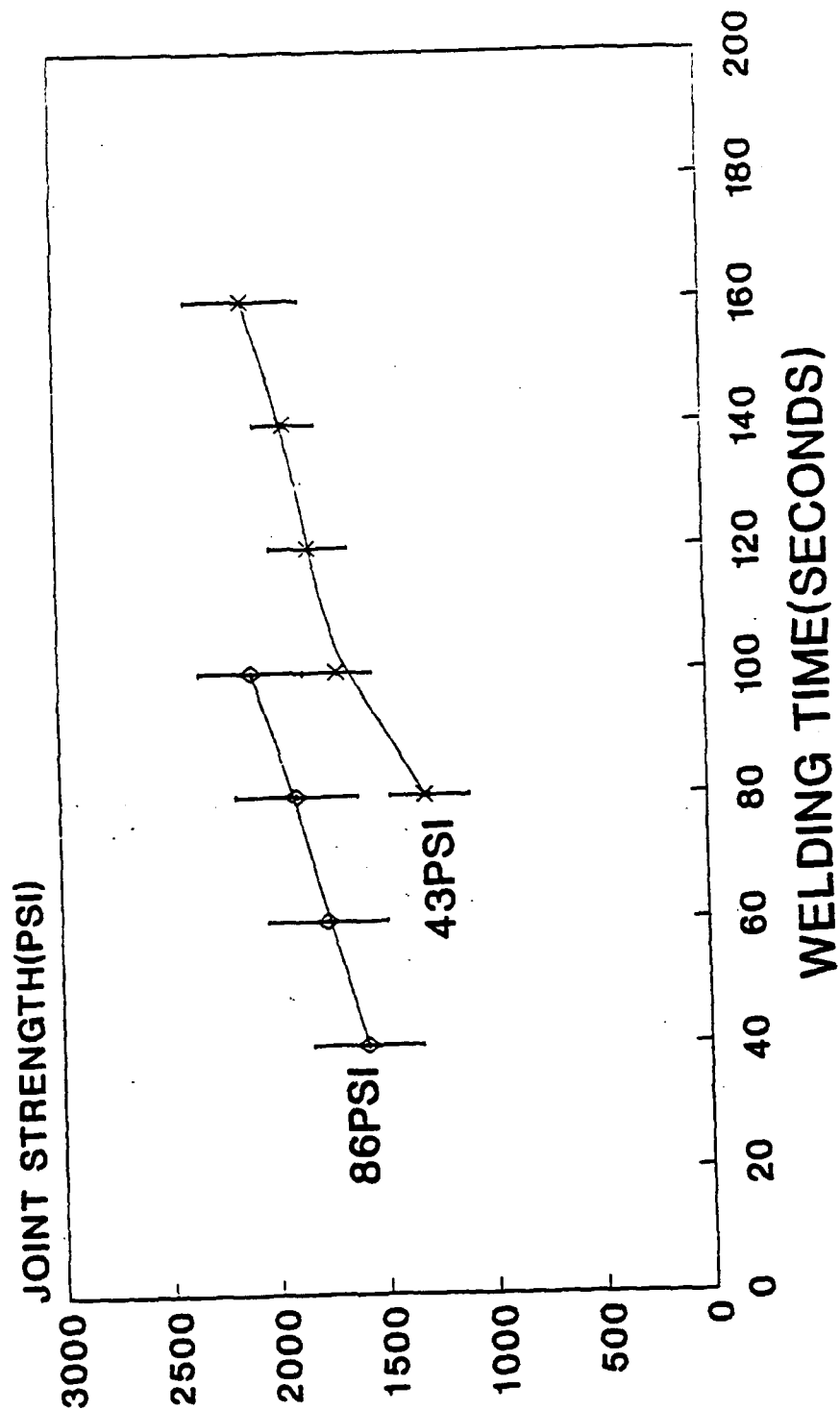
Frequency (GHz)

II-B-112

MICROWAVE WELDING HDPE

EFFECT OF PRESSURE

50%PAN THICKNESS=20MILS

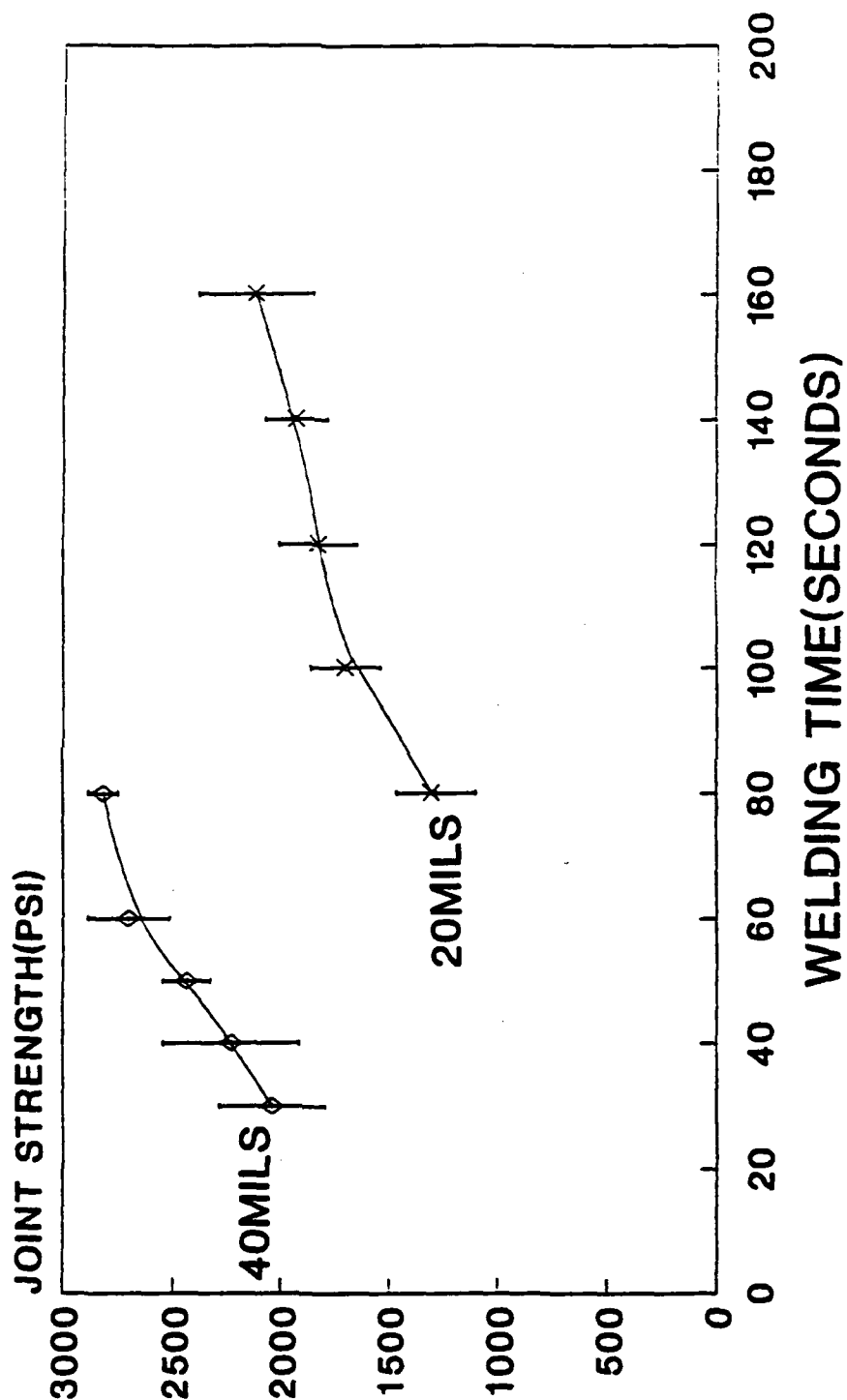


PRESSURE

MICROWAVE WELDING HDPE

EFFECT OF THICKNESS

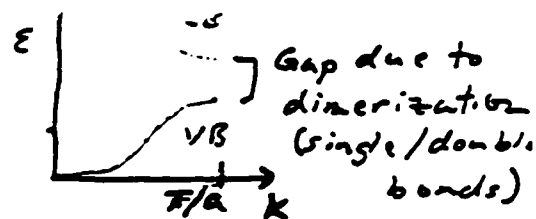
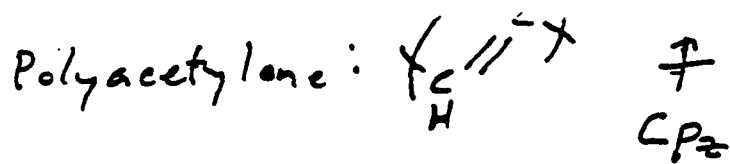
50%PAN PRESSURE=43PSI



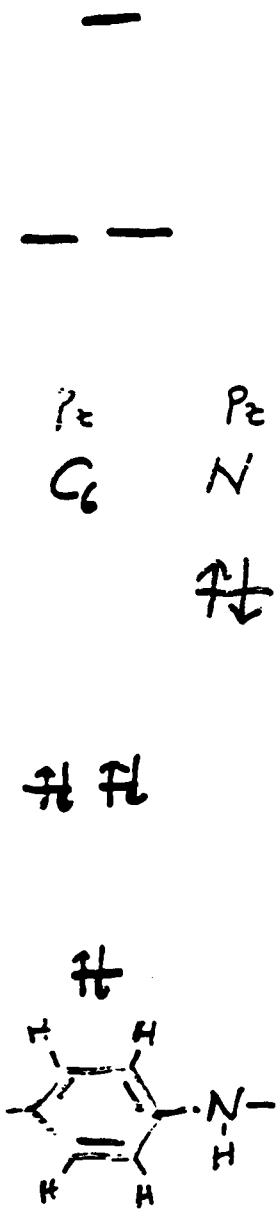
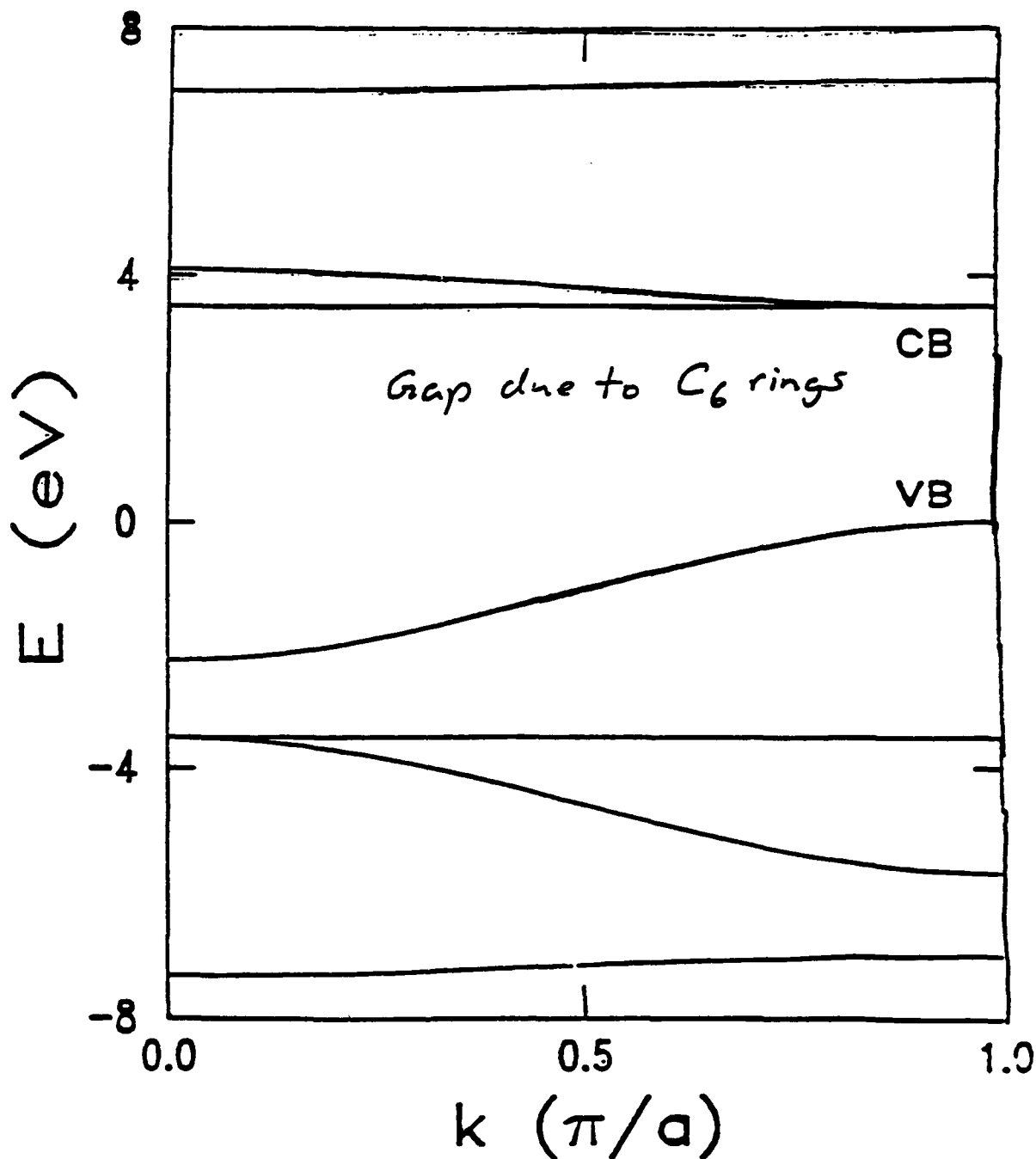
THICK

**TORSION ANGLE DEFECTS
AND
BOND LENGTH DEFECTS
IN POLYANILINE**

II-B-115



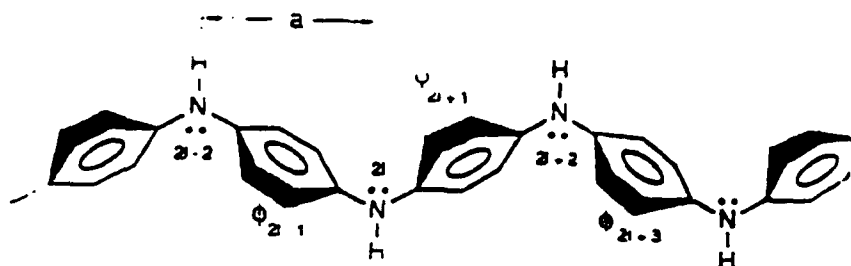
Leucoemeraldine (polyaniline):



Ginder, et al., Fig. 2

HÜCKEL MODEL FOR LB

A Generalized A-B Polymer



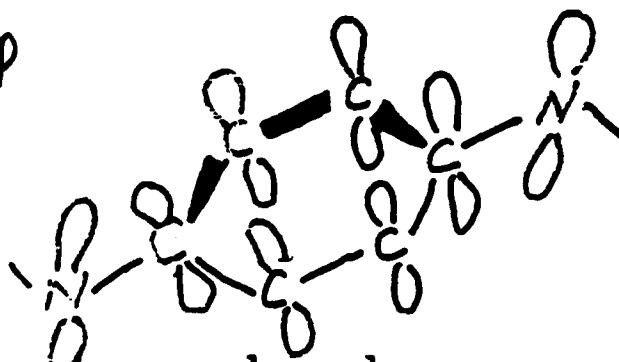
- Model Hamiltonian:

$$H_{el} = \sum_{l,s} \alpha_N a_{2l,s}^\dagger a_{2l,s} + \sum_{l,s} \sum_j \epsilon_j b_{2l+1,s}^\dagger b_{2l+1,s} + \sum_{l,s} \sum_j [t_{2l,2l+1}^\dagger (a_{2l,s}^\dagger b_{2l+1,s}^\dagger + b_{2l+1,s}^\dagger a_{2l,s}^\dagger) + t_{2l+1,2l+2}^\dagger (b_{2l+1,s}^\dagger a_{2l+2,s}^\dagger + a_{2l+2,s}^\dagger b_{2l+1,s}^\dagger)]$$

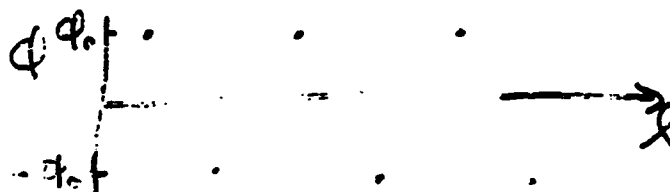
CHARGE TRANSFER

- Electron-ring-angle coupling:

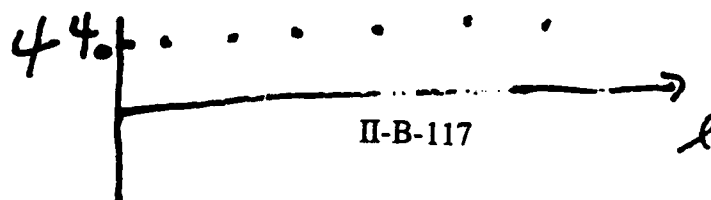
$$t_{AC} = t_0 \cos \phi$$

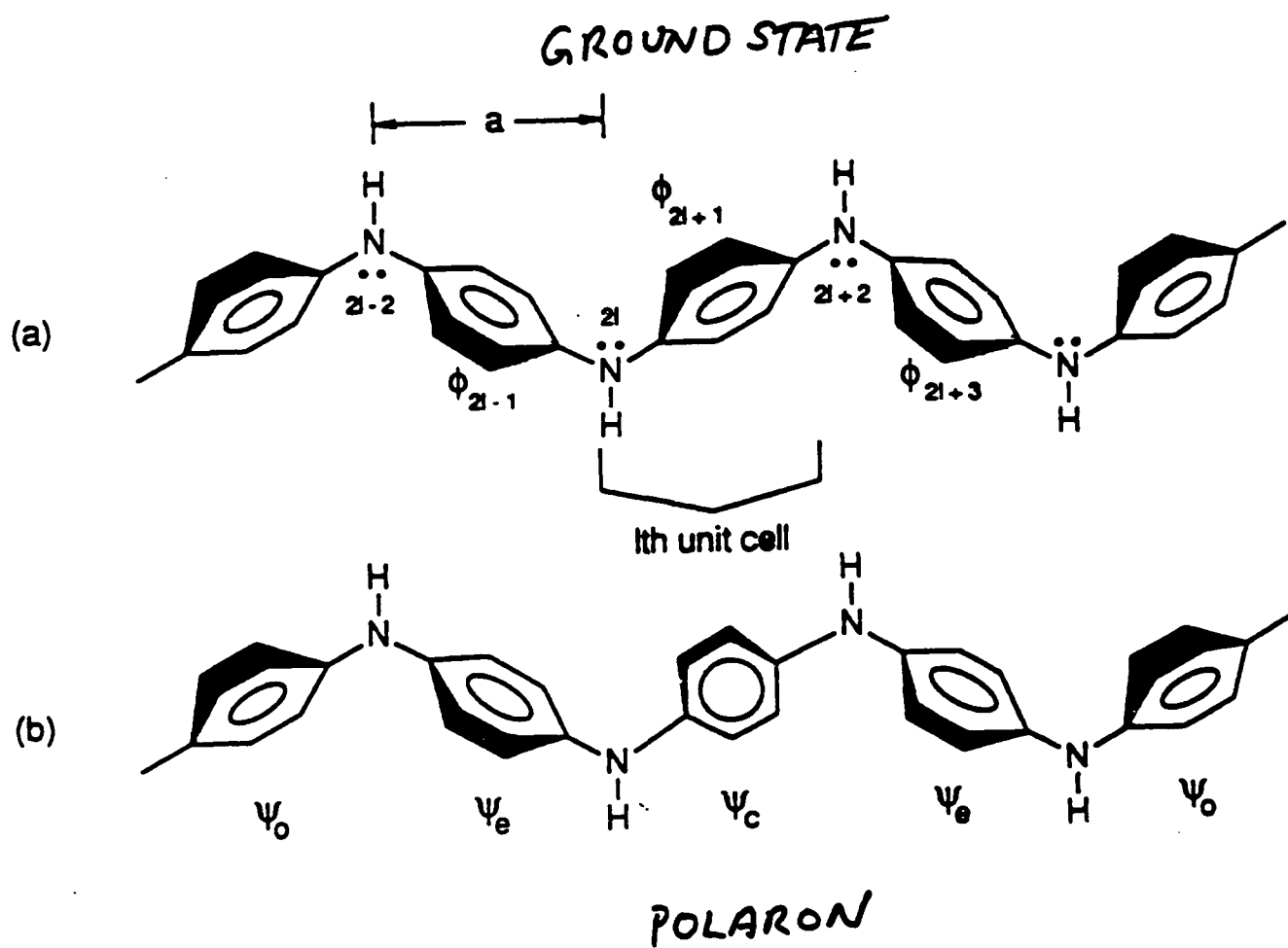


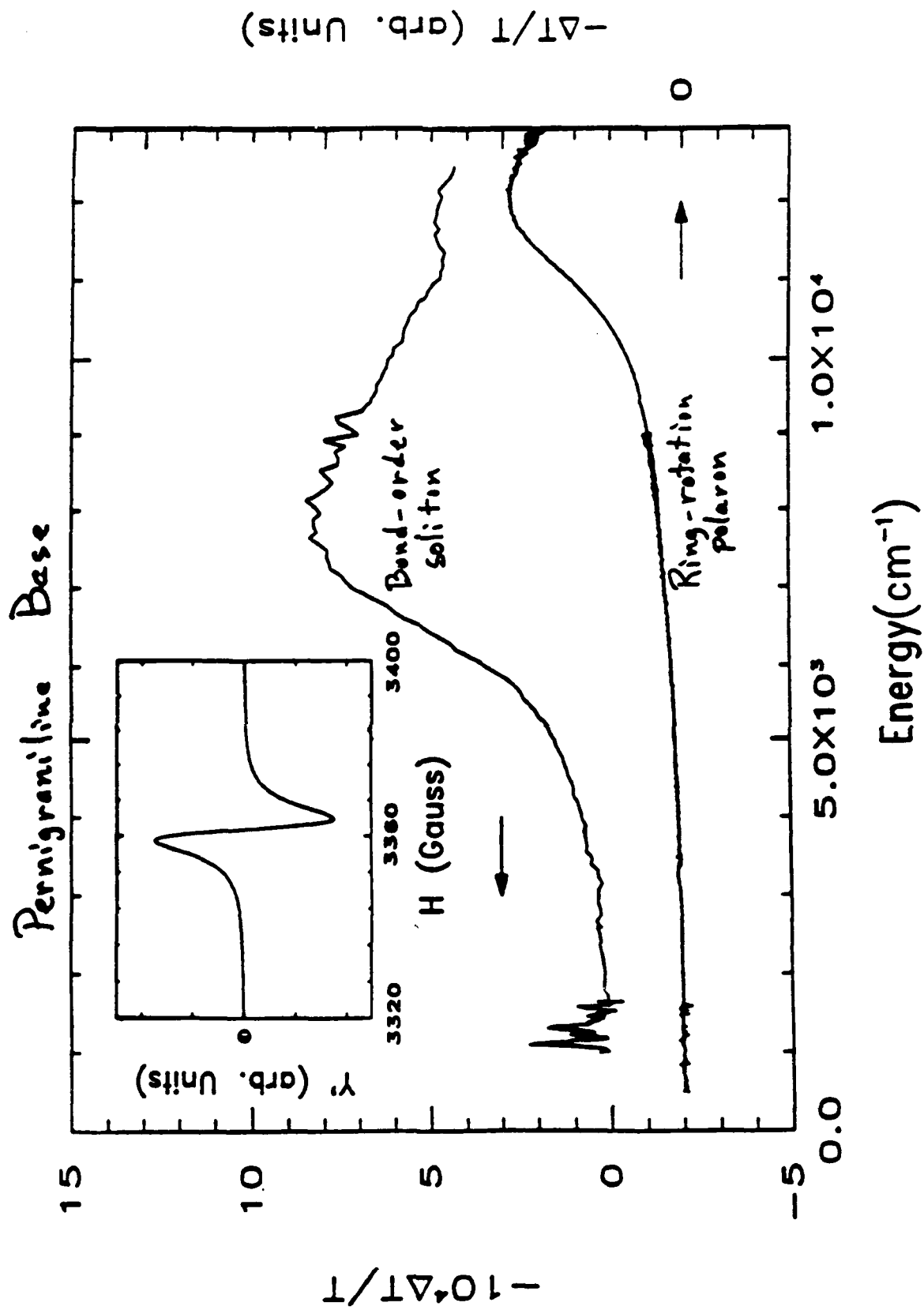
- Ring-torsion-angle order parameter



$$\phi_{2l+1} = (-1)^l \phi_{2l+1}$$

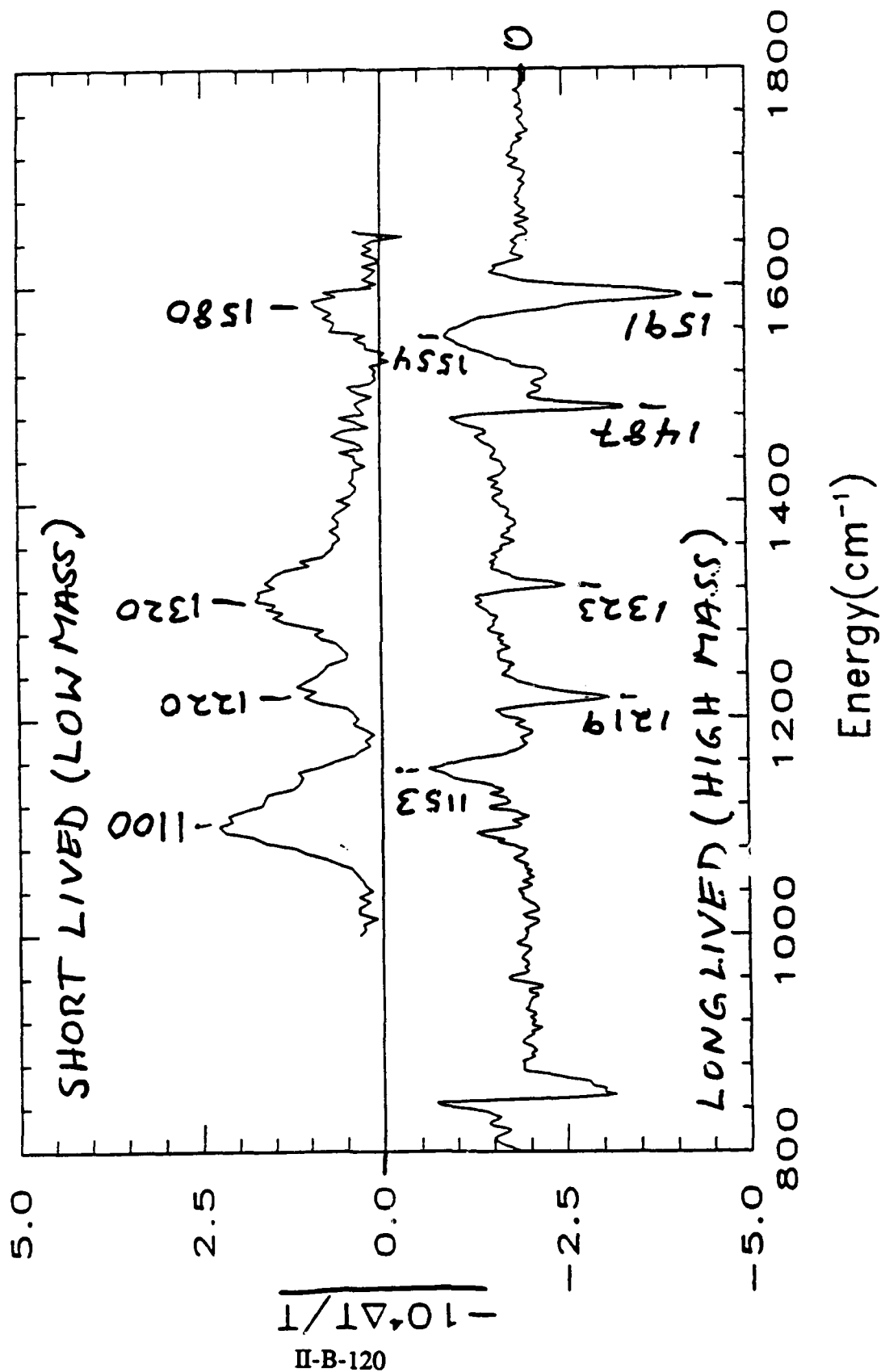






● Peierls state in Pernigraniline Base

PHOTO INDUCED I.R. A.



DETERMINATION OF DEFECT MASS (M_D)

- Determine M_D for various derivatives of different oxidation states of polyaniline (EB, PNB)
- Amplitude Mode Formalism
(Horovitz, SSC 41 729, (1982); Ehrenfreund et al. PRB 36 1535 (1987).)

$$\underline{I_v} = \frac{\pi \rho e^2}{2 \underline{M_D}}$$

I_v = integrated intensity of photoinduced vibrational absorptions
 ρ = density of charged defects

$$\underline{I_e} = \frac{2.8 \rho e^2}{\underline{m^*}}$$

I_e = integrated intensity of electronic absorptions at 1.4 and 3.0 eV
 $m^* = \hbar^2 (\partial^2 E / \partial k^2)^{-1} \sim 0.14 m_e$

$$\underline{M_D} = \frac{\pi m^* \underline{I_e}}{5.6 \underline{I_v}}$$

- Determine relationship between M_D and moment of inertia of substituted ring
- Determine relationship between M_D and lifetime of defect

NO-A257 309

THE DARPA HIGH-PERFORMANCE POLYMER PROGRAM VOLUME 2

3/8

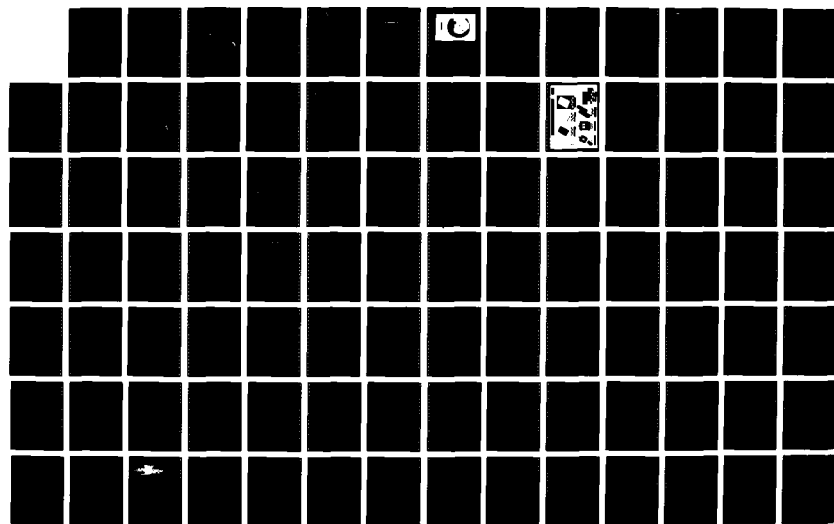
APPENDIX--SELECTED PR. (U) INSTITUTE FOR DEFENSE

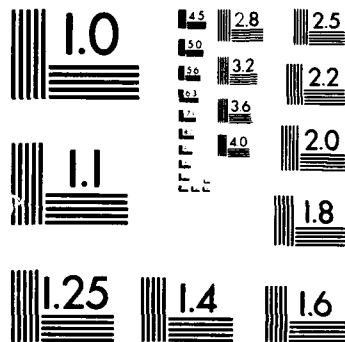
ANALYSES ALEXANDRIA VA D R SQUIRE ET AL. SEP 92

UNCLASSIFIED

IDA-D-1174-VOL-2 IDA/HQ-92-42533

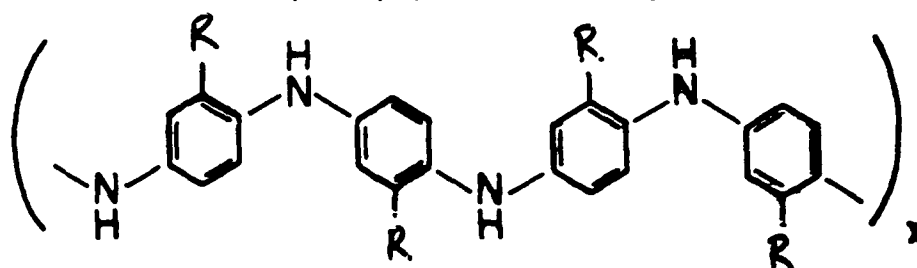
NL



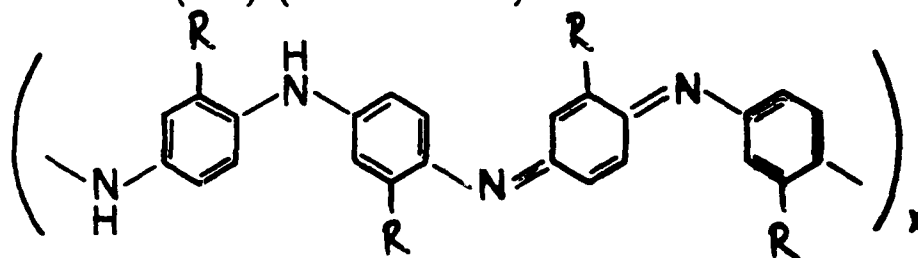


POLYANILINE FAMILY

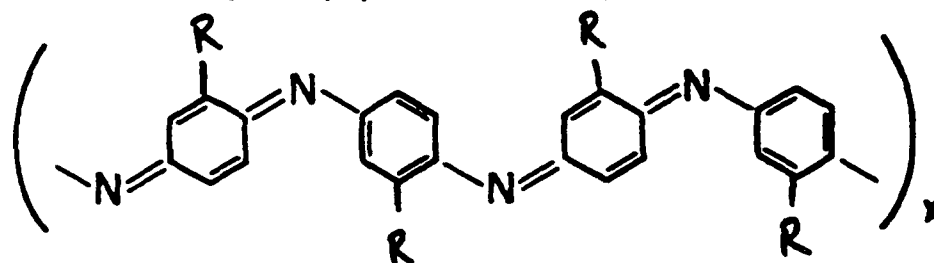
Leucoemeraldine Base (LEB) (fully reduced)



Emeraldine Base (EB) (half-oxidized)



Pernigraniline Base (PNB) (fully oxidized)



R = H

polyaniline

R = CH₃

poly(*o*-toluidine)

POT (Methyl)

R = C₂H₅

poly(2-ethylaniline)

ETHYL

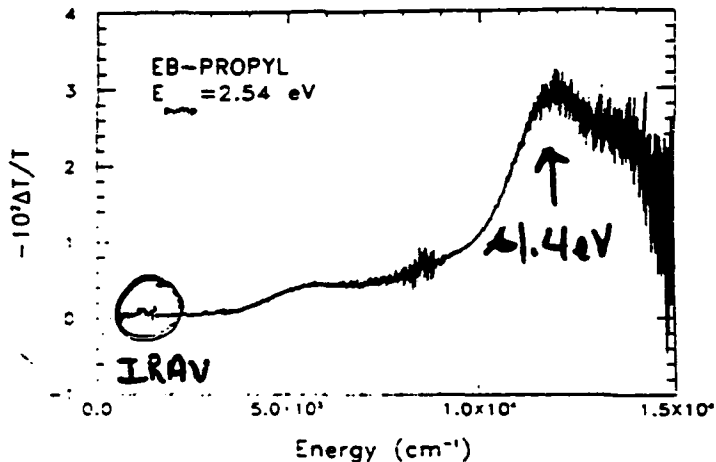
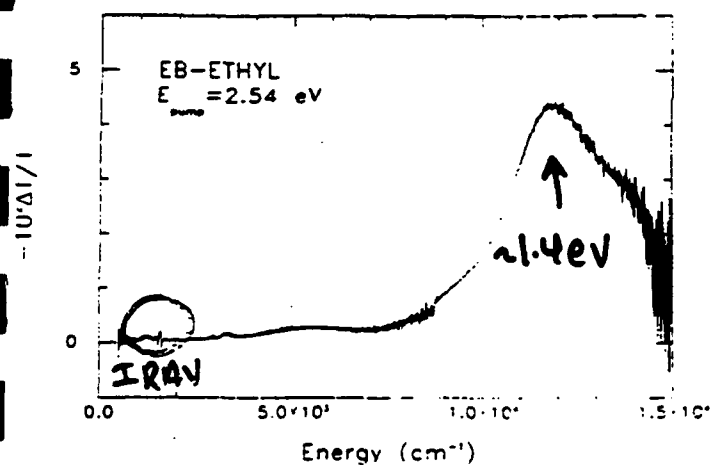
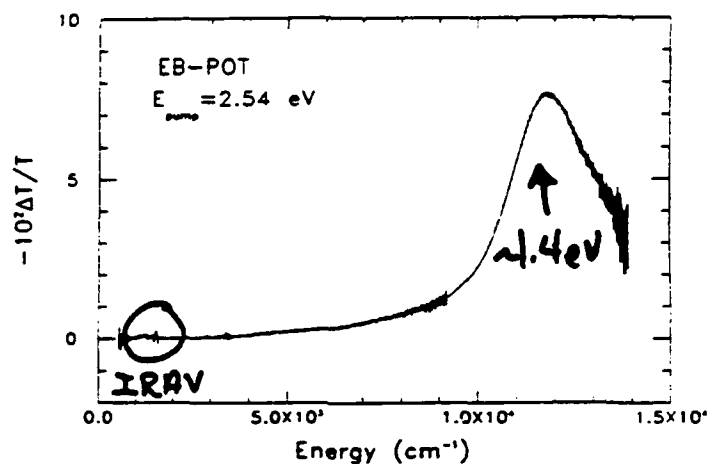
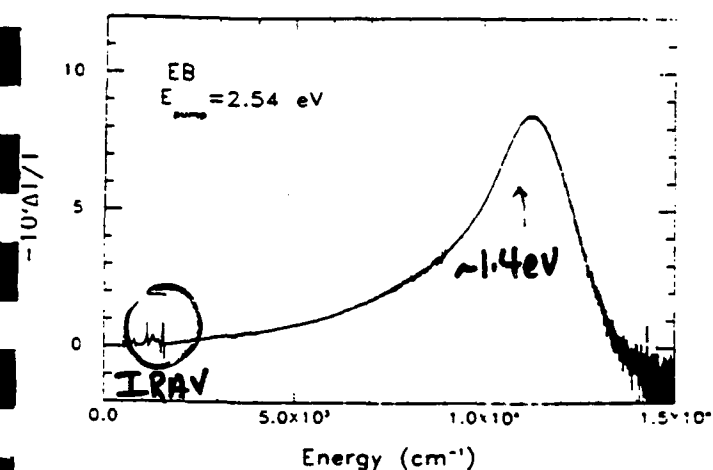
R = C₃H₇

poly(2-propylaniline)

PROPYL

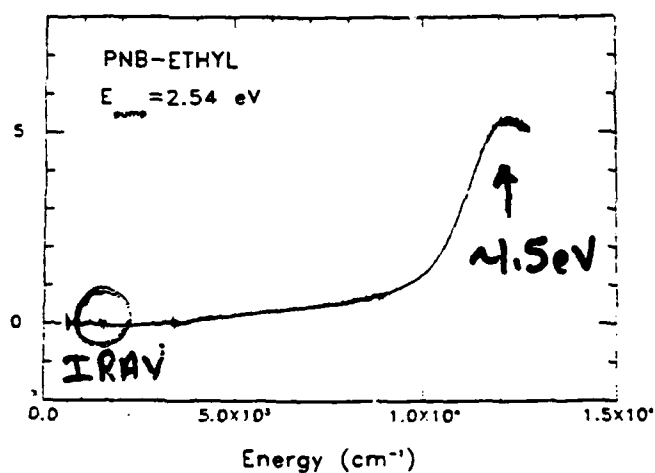
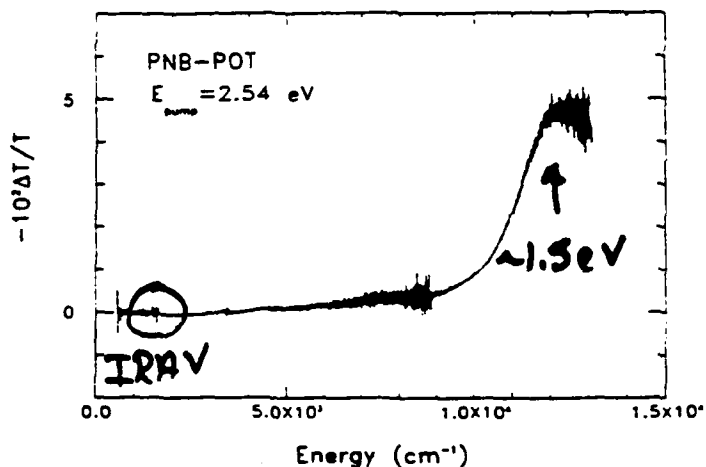
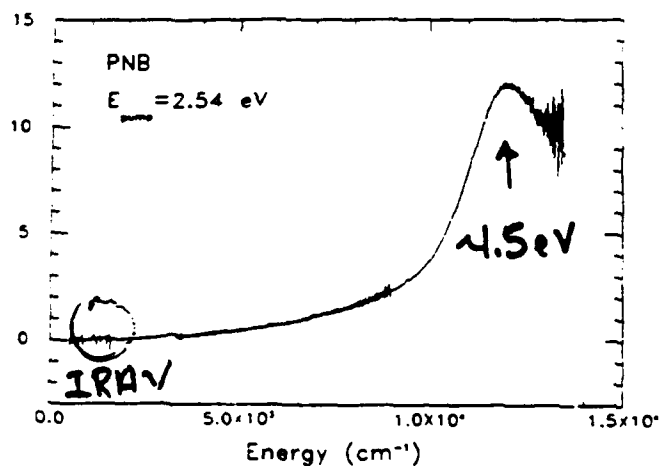
- e.g., EB-POT is half-oxidized poly(*o*-toluidine).

RESULTS FOR EMERALDINE OXIDATION STATE



Material	I_e/I_v	M_D
EB	~650-750	~50-60 m_e
EB-POT (methyl)	~1600-1800	~130-140 m_e
EB-ETHYL	~1600-1800	~130-140 m_e
EB-PROPYL	~1300-1800	~100-130 m_e

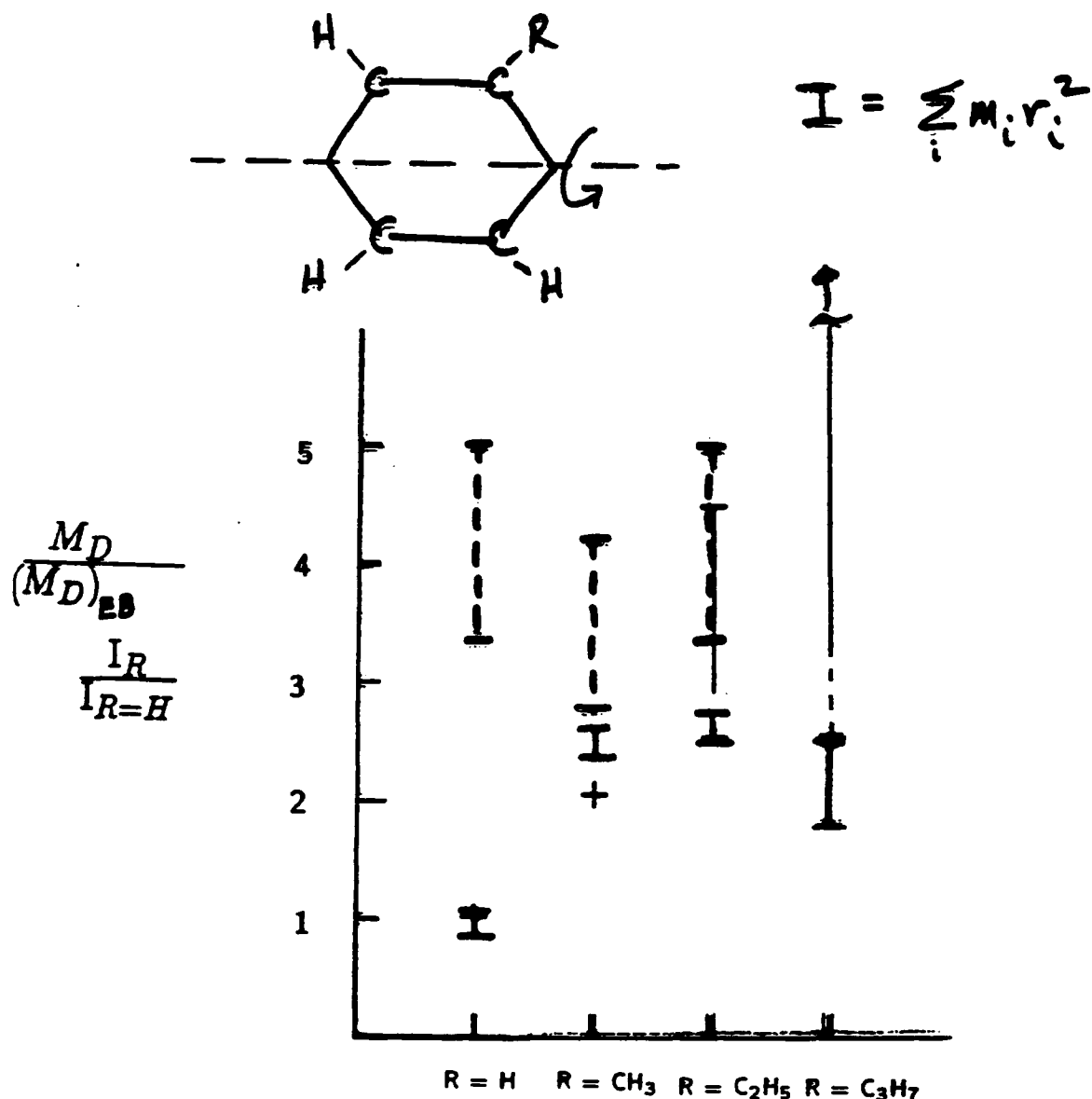
RESULTS FOR PERNIGRANILINE OXIDATION STATE



K. Coplin
R. McCall

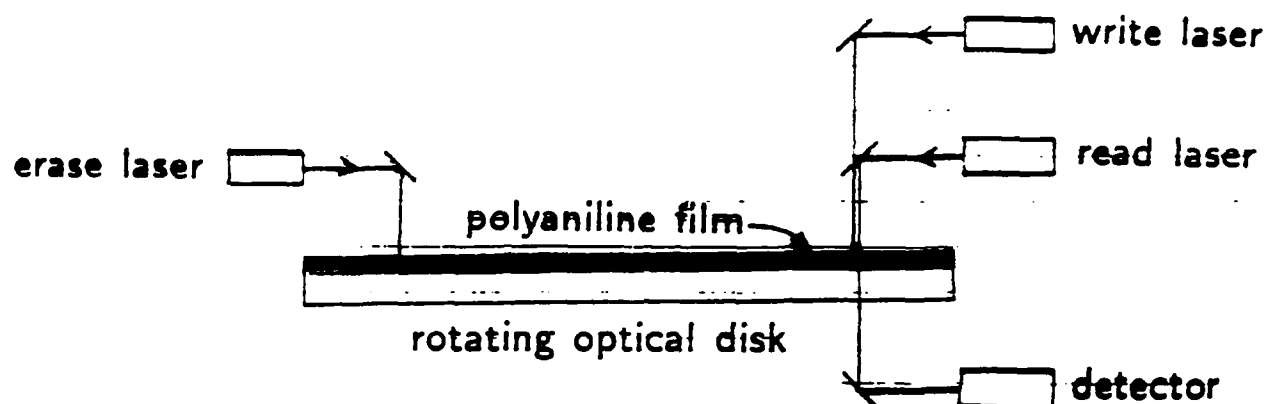
Material	I_e/I_v	M_D
PNB	~2500-3800	~200-300 m_e
PNB-POT (methyl)	~1900-3200	~150-250 m_e
PNB-ETHYL	~2500-3800	~200-300 m_e

RELATIONSHIP BETWEEN DEFECT MASS (M_D) AND MOMENT OF INERTIA (I)



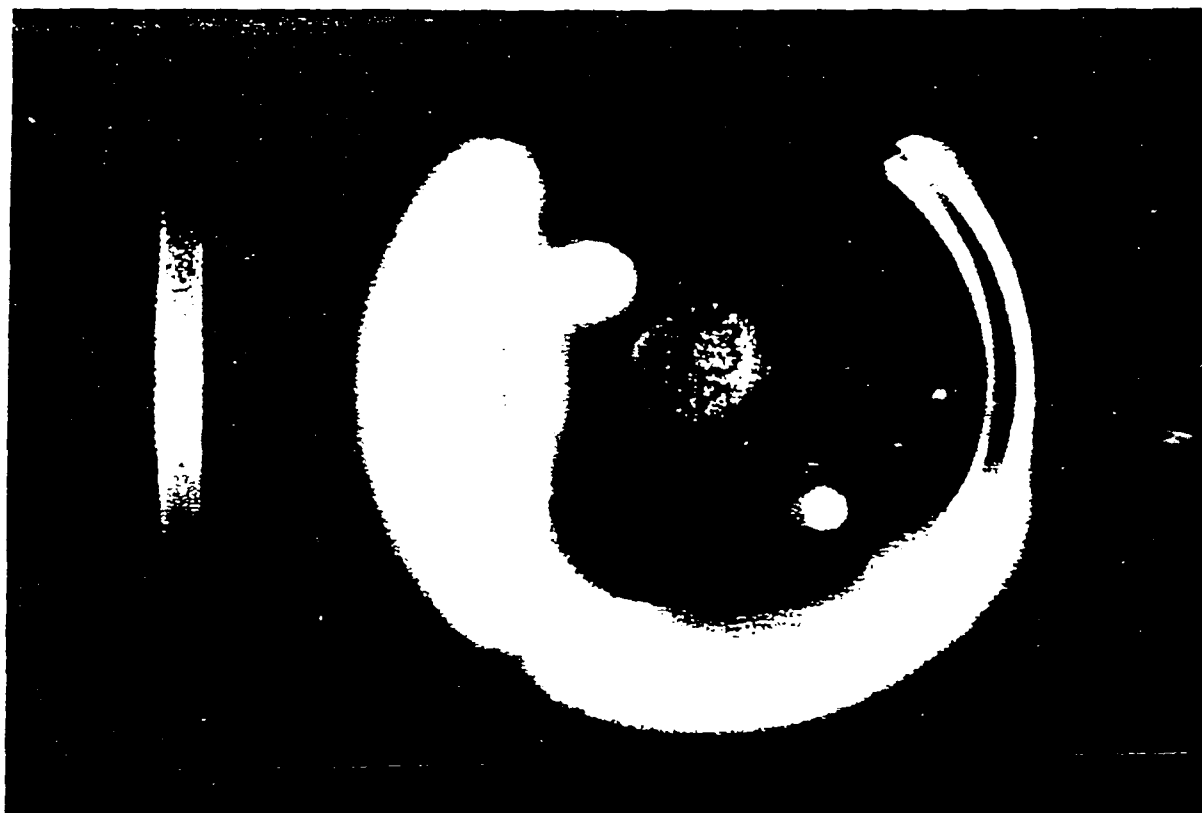
- EB— M_D increases then constant
- PNB— M_D constant and larger than expected
- Variation in M_D cannot be explained only by variation in I
- Variation in steric potential (interchain and intrachain interactions) likely contributes to this behavior

SCHEMATIC DEVICE CONFIGURATION:



IDEALIZED PARAMETERS:

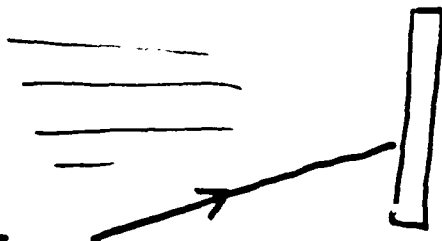
- Bit size diffraction limited: $\sim 1\mu\text{m}$
- Energy density for writing $\lesssim 10 \text{ nJ}/\mu\text{m}^2$
- High write/erase cyclability expected because no bonds are broken.
- Operating temperature currently at -25°C ; new compositions may allow for increase to 50°C .
- Signal-to-noise $>20 \text{ dB}$ (20 kHz bandwidth)
- Multiple read and write energy bands are available.
- Polymer can be used as a thin film on a substrate or in a matrix.
- Chemical tunability for lifetime, processing, and compatibility.



READ
LAMP

(9)

WRITE
LASER



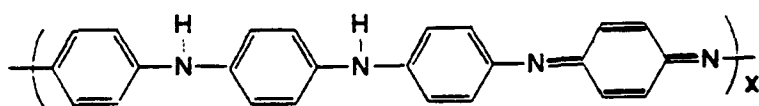
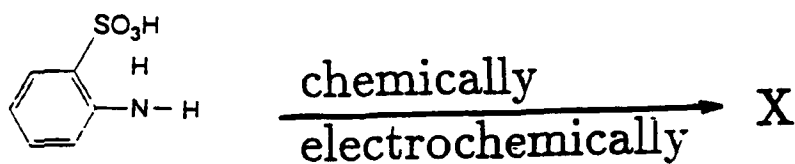
SAMPLE



CAMERA
WITH INERARED
FILM

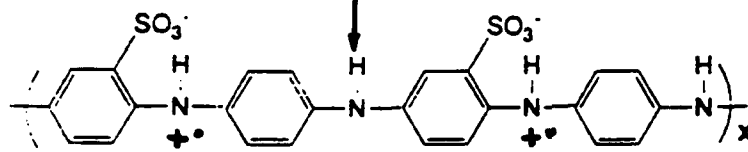
**SULFONIC ACID DERIVITIZED
POLYANILINE:
NH₃ PHENOMENA
pH MODULATION**

SYNTHESIS



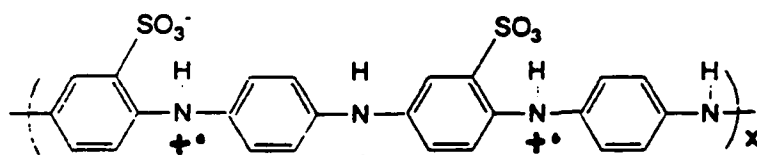
emeraldine base

$\text{H}_2\text{SO}_4(\text{SO}_3)$



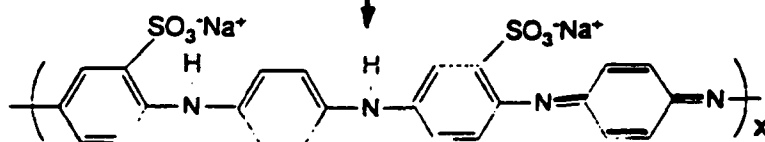
sulfonated
emeraldine

(soluble in basic aqueous solutions)



sulfonated
emeraldine

0.1 M NaOH

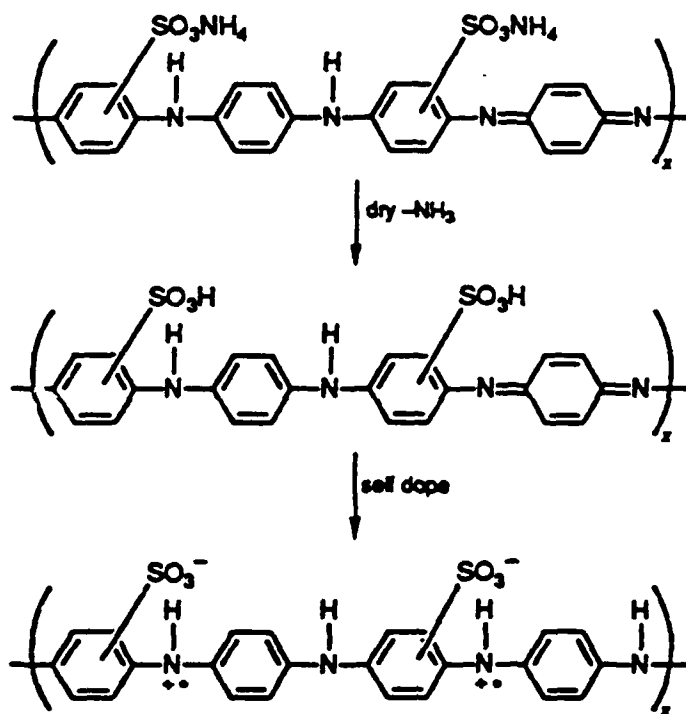


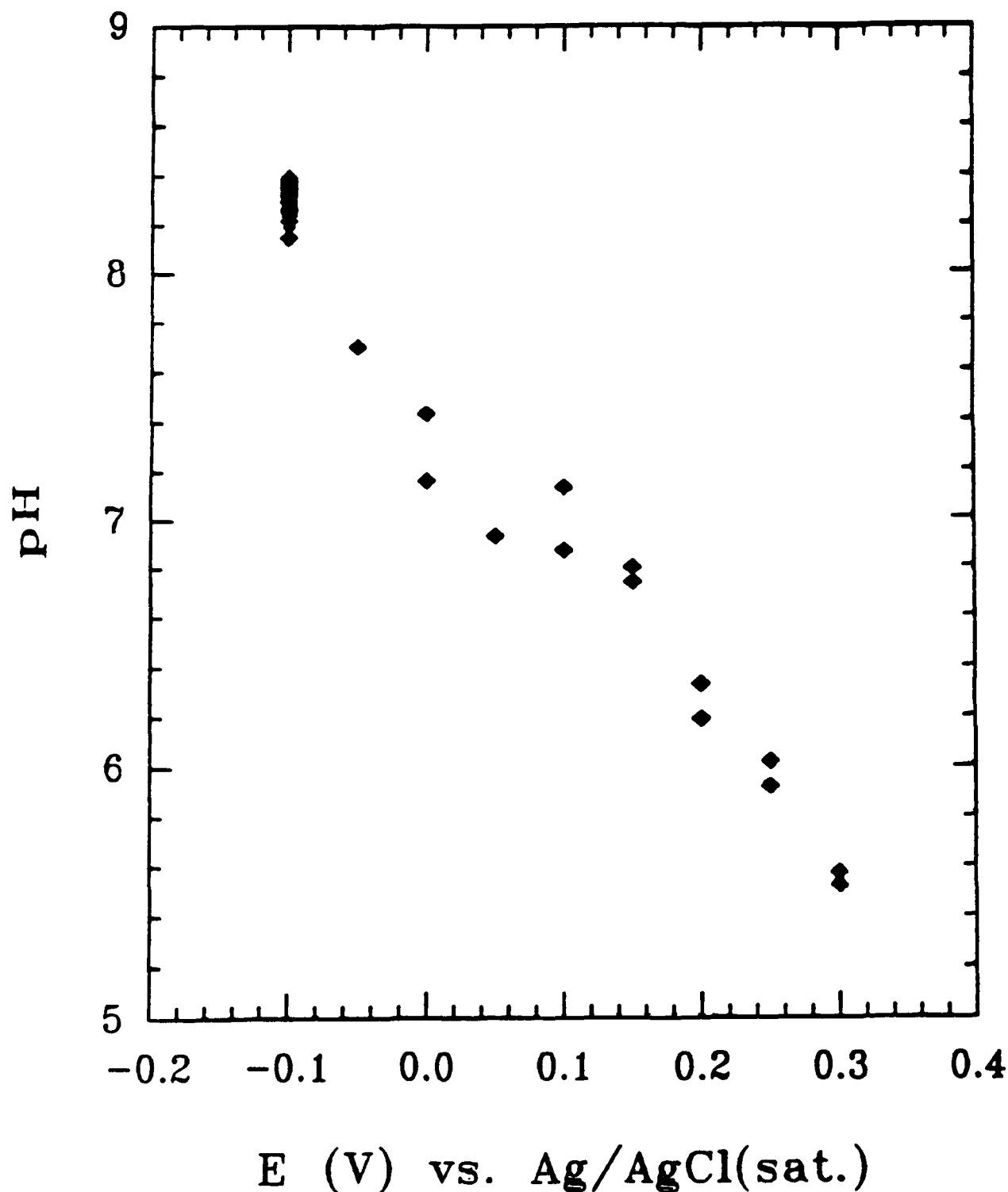
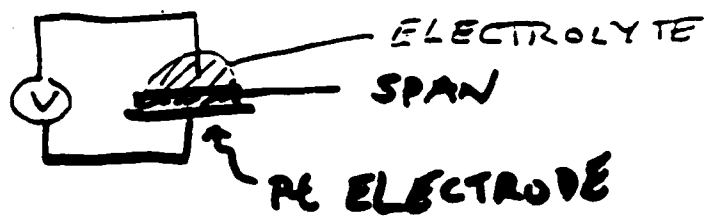
Na salt of
SPAN
(EB backbone)

(soluble in water)

Sulfonic Acid Group Effect on Polyaniline Backbone

Conversion of Ammonium Salt of Polymer I to Its Self-Doped Conducting Form





E (V) vs. Ag/AgCl(sat.)

VOLTAGE CONTROL OF pH

MONITORING & MODULATION OF ENZYME ACTIVITY

FUTURE PLANS

- Extend studies of microwave properties of polyanilines and blends
- Controlled welding of thermoplastic joints using polyaniline and blends
- Determination of lifetime of photoinduced defects in derivatives
- Electrochemical control of enzymes
- Explore ultimate conductivity of polyanilines



CONDUCTING ELECTRONIC POLYMERS BY NON-REDOX PROCESSES

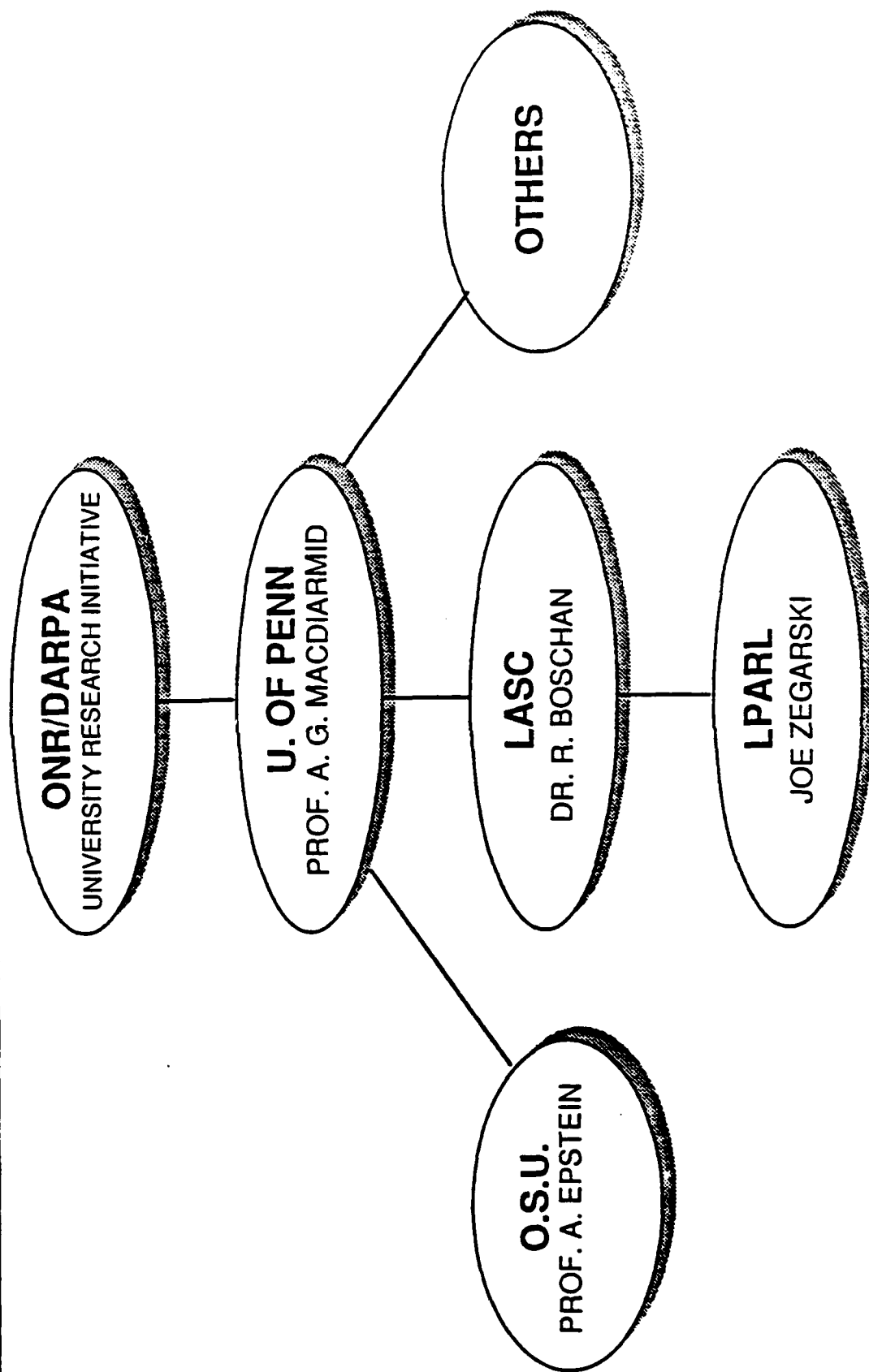
Joe Zegarski

**Lockheed Palo Alto Research Laboratory O/93-50
B/204; 3251 Hanover St.; Palo Alto, CA 94304
415-424-2192**

January 14, 1992



LOCKHEED SUBCONTRACT ORGANIZATION





OBJECTIVES

Overall Objective

Identify and investigate aerospace applications for university research

Technical Objective

Demonstrate feasibility of using conducting polymers in welding/joining of thermosets and thermoplastics



ELECTROMAGNETICALLY INDUCED WELDING/JOINING USING CONDUCTIVE POLYMERS

PROCESS CONSIDERATIONS

Conductive Polymer

EM absorption, reflection;
conductivity; undoping
temperature

EM power & frequency
Pressure applied to sample

Microwave/Induction

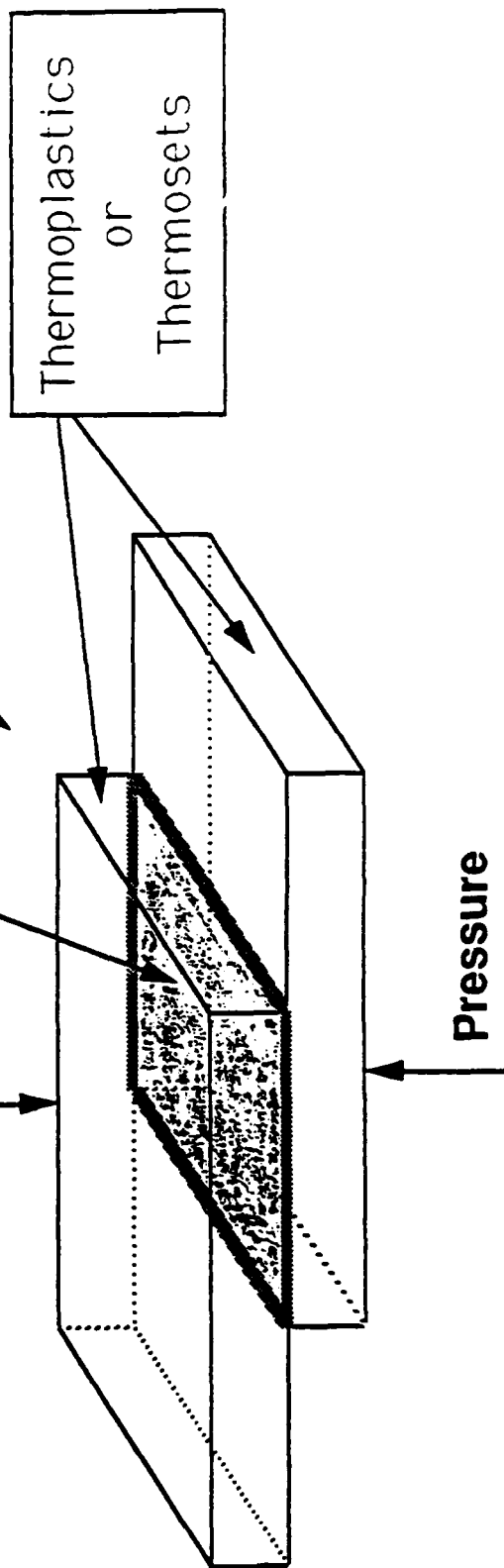
Energy

Conducting
Polymer

Pressure

Thermoplastics
or
Thermosets

Pressure





ELECTROMAGNETICALLY INDUCED WELDING/JOINING USING CONDUCTING POLYMERS

Potential applications

- Fabrication processes
- Field repair
- Motivation: time savings

Systems Using Composites

- Aircraft: Stealth Fighter, Advanced Tactical Fighter
- Missile: Motor cases on Navy FBM systems
- Space: struts for space station
- Marine: composite submarine hulls



ELECTROMAGNETICALLY INDUCED WELDING/JOINING USING CONDUCTING POLYMERS

Relevance

- DoD Critical Technologies Plan - 1990
Processing of reinforced epoxies and PEEK
- Research & Technology Objectives & Plans Summary
NASA Lewis Research Center - NASA TM-103086
Conductive polymer composites
- Army Aviation RDT&E Plan - FYs 1988-95
Develop novel curing techniques for composite field repair
Develop rapid, low-energy concepts for curing composites



ADVANTAGES OF CONDUCTING POLYMERS

- Density
- Coefficient of thermal expansion

CTE (/ °K)

Nylon-6/6	1.2×10^{-4} (a)
Epoxy	6.0×10^{-5} (b)
Polyaniline	1.0×10^{-4} (b)
Carbon fibers (axial)	-1.0×10^{-6} (a)
Carbon fibers (transverse)	7.8×10^{-6} (a)

- Tailorable properties
 - Conductivity
 - Undoping temperature
 - Self-regulating heating element

- (a). Engineered Materials Handbook, vol. 1, ASM International, United States (1987).
(b). Electrically Conductive Organic Polymer for Advanced Applications, ed.(Noyes Data Corporation, New Jersey), 1986.



TECHNICAL PLAN

1992 →

Plan and Schedule

Literature search

Identify aerospace applications

Materials/equipment acquisition

Welding of thermoplastics

Welding of thermosets

Mechanical testing

Microscopy analysis

Quarterly Reports

<u>O</u>	<u>N</u>	<u>D</u>	<u>J</u>	<u>F</u>	<u>M</u>	<u>A</u>	<u>M</u>	<u>J</u>
XXXX								
XXXX								
XXXXXXXXXX								
		XXXXXXXXXXXXXXXXXXXX						
				XXXXXXXXXXXXXXXXXXXX				
			XXXXXXXXXXXXXXXXXXXX					
					XXXXXXXXXXXXXXXXXXXX			
						XXXXXXXXXXXXXXXXXXXX		
			X				X	X

Lockheed LPARL TECHNICAL PROGRESS SINCE SEPT. 1991
SUMMARY

- Obtained materials and equipment
- Fabricated all-plastic rig for applying known pressures
 - Calibrated against load cell
- Prepared conductive polymer films
 - Free-standing and painted films
 - Measured surface resistance
- Welded Nylon and performed tensile-strength tests of bond line
- Joined together two pieces of fiberglass-epoxy

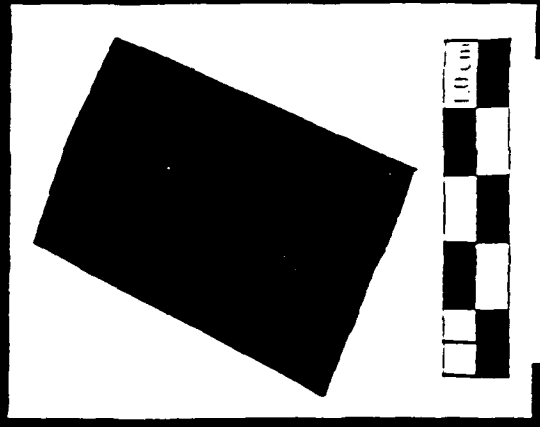


WELDING OF NYLON-6/6

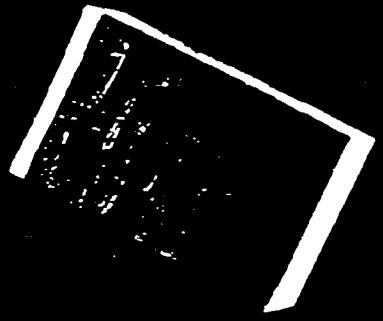
- Demonstrated welding using:
Versicon powder
Versicon/Nylon films made at LPARL
- Nylon melts only at weld joint; no heating of bulk
- Best result to date: 1500 psi tensile strength of bond line
- Undoping temperature of Versicon is comparable to melt temperature of Nylon-6/6
- Shows need for Penn high-temperature polyanilines

Microwave-Induced Welding of Thermoplastics Using Conductive Polymers

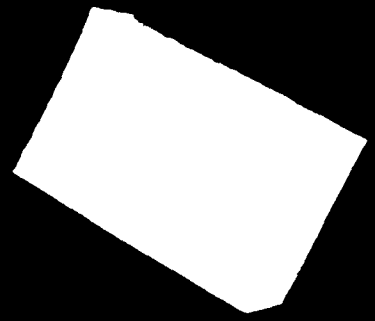
II-B-143



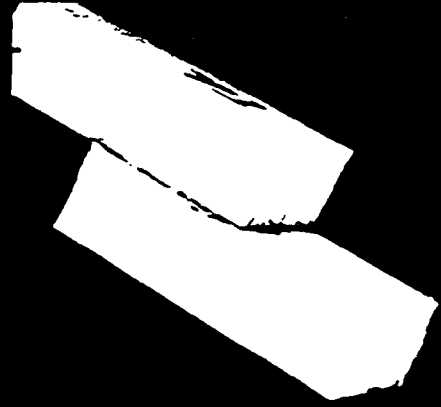
Versicon/Nylon (50-50) film
2.5 mils thick



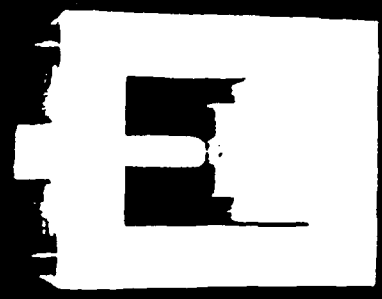
Nylon 6/6 coated with
Versicon Nylon 11:1 paint



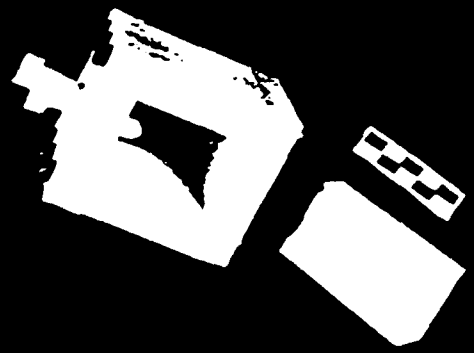
Nylon 6/6
1.5" x 2.5" x 0.75"



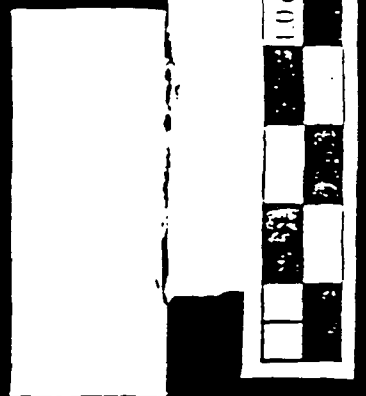
Welded Nylon pieces



Rig for applying pressure to
samples during welding



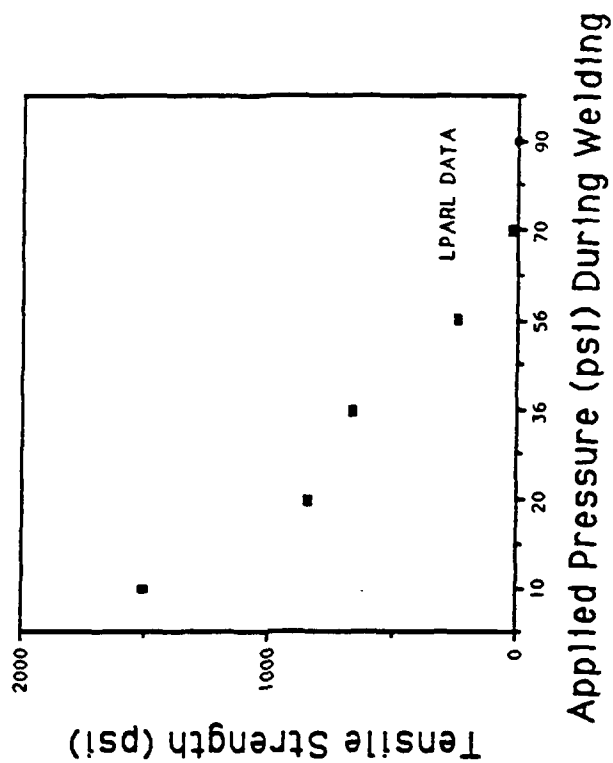
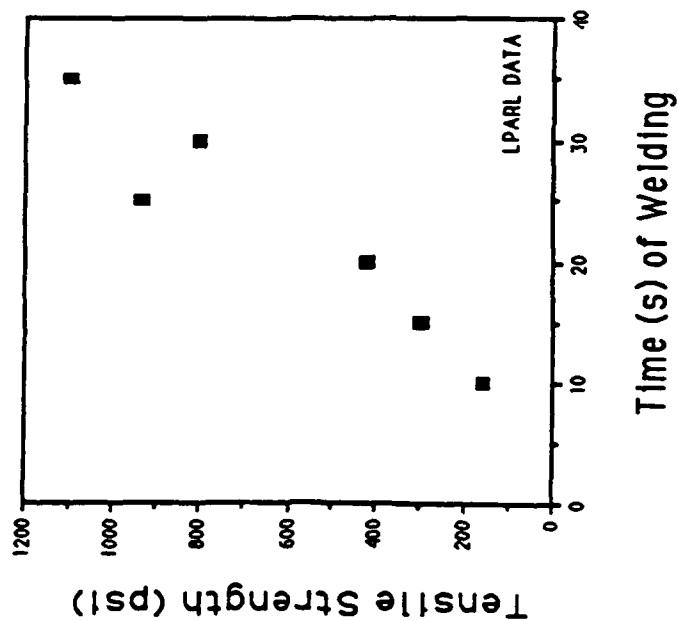
Rig for applying pressure to
samples during welding



Welded Nylon pieces



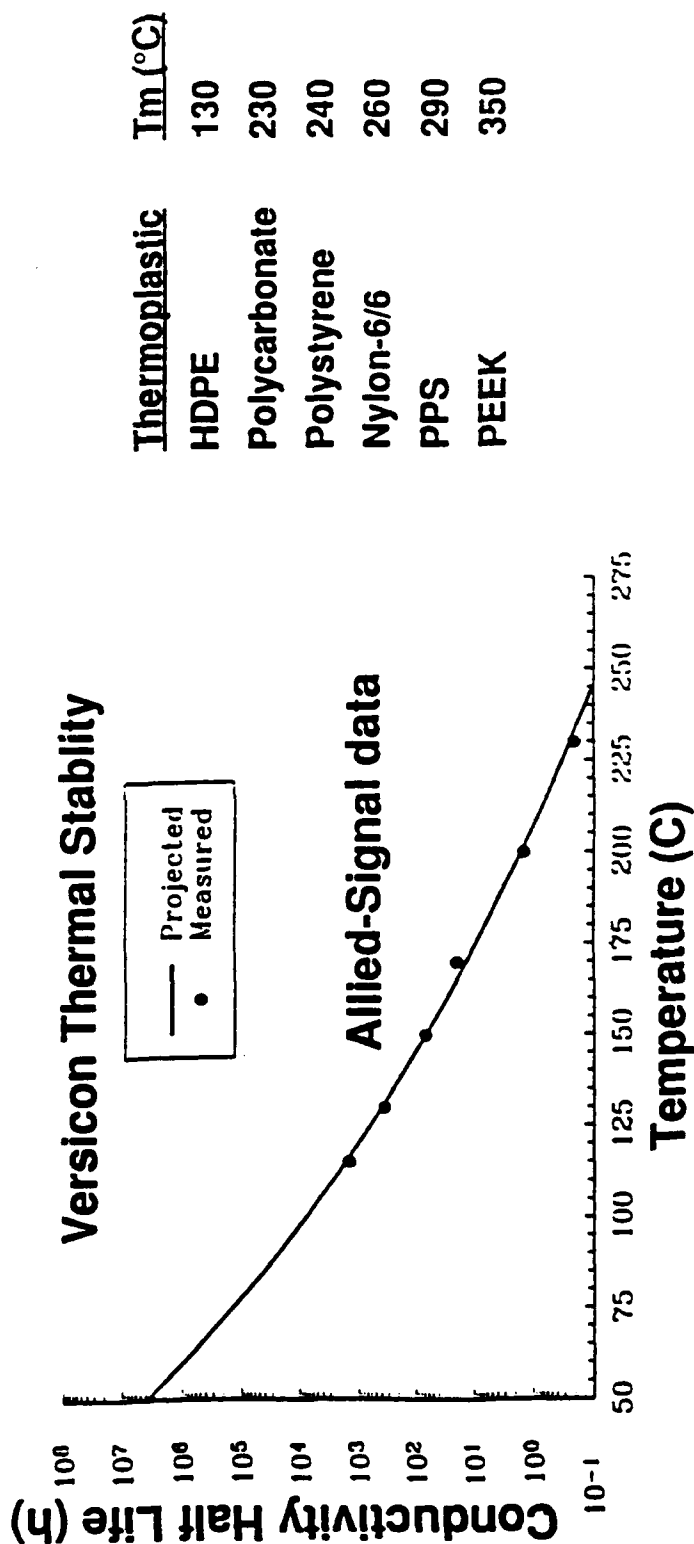
TENSILE-STRENGTH TESTS OF WELD JOINT





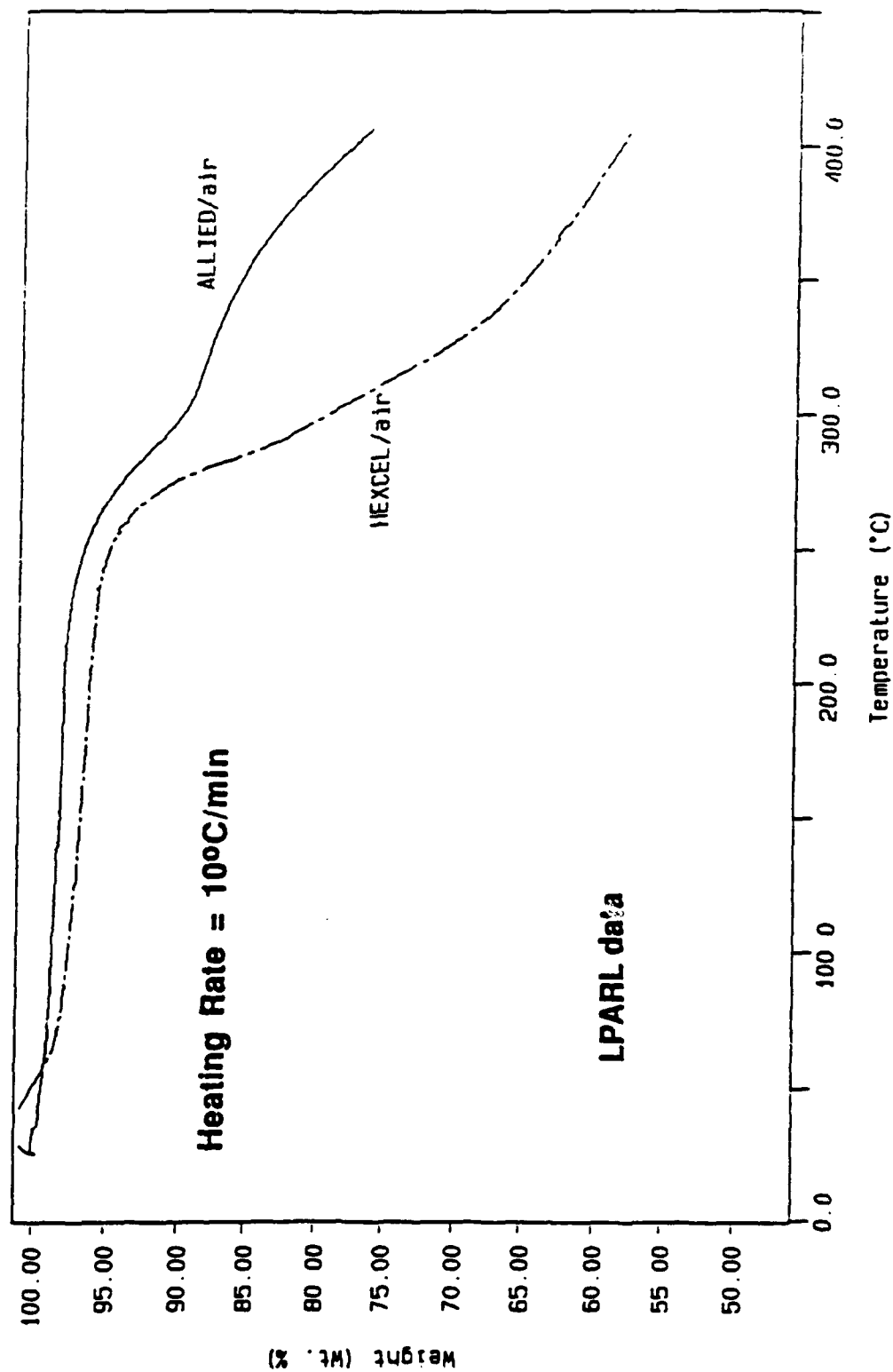
VERSICON: A COMMERCIALLY AVAILABLE POLYANILINE

- Available from Allied-Signal, Inc.
- Evolves organic acid dopant upon undoping
- Short half-life of conductivity at temperatures above 250°C





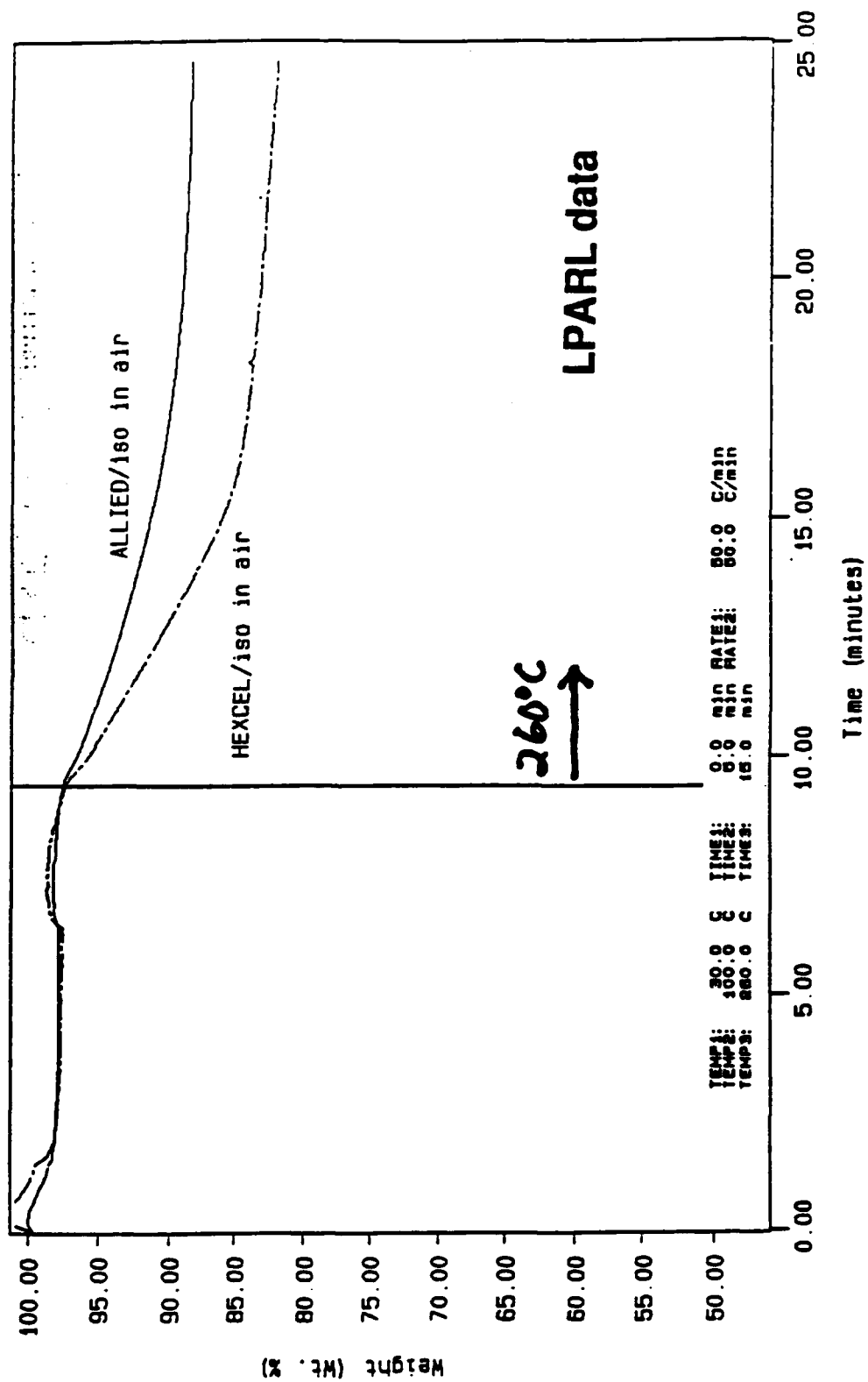
TGA OF VENDOR-SUPPLIED POLYANILINES



II-B-146



TGA OF VENDOR-SUPPLIED POLYANILINES

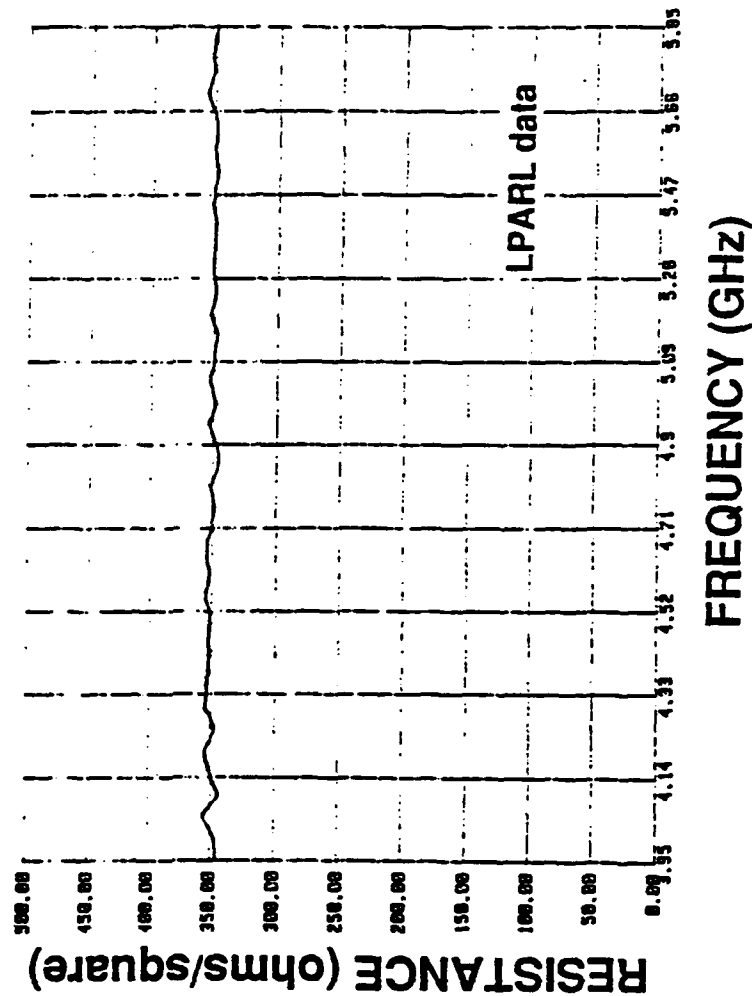


II-B-147



MICROWAVE SURFACE RESISTANCE

- Derived from reflection scattering parameter S11
- HP8510B network analyzer

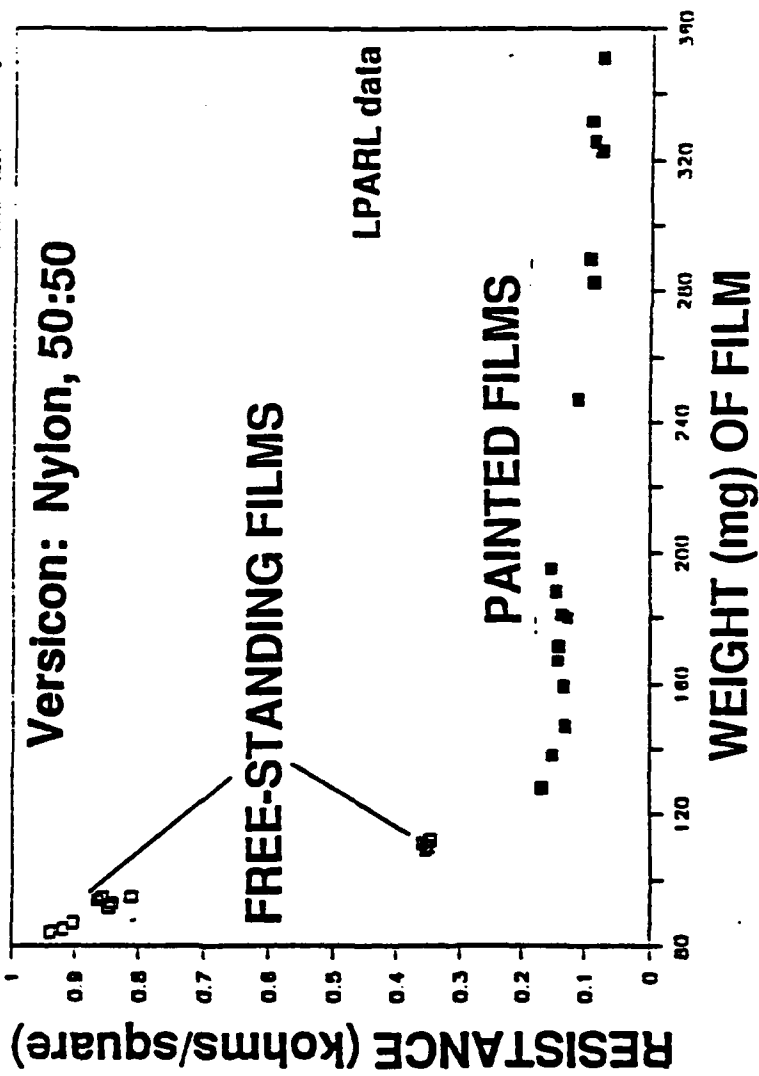




VERSICON/NYLON FILMS

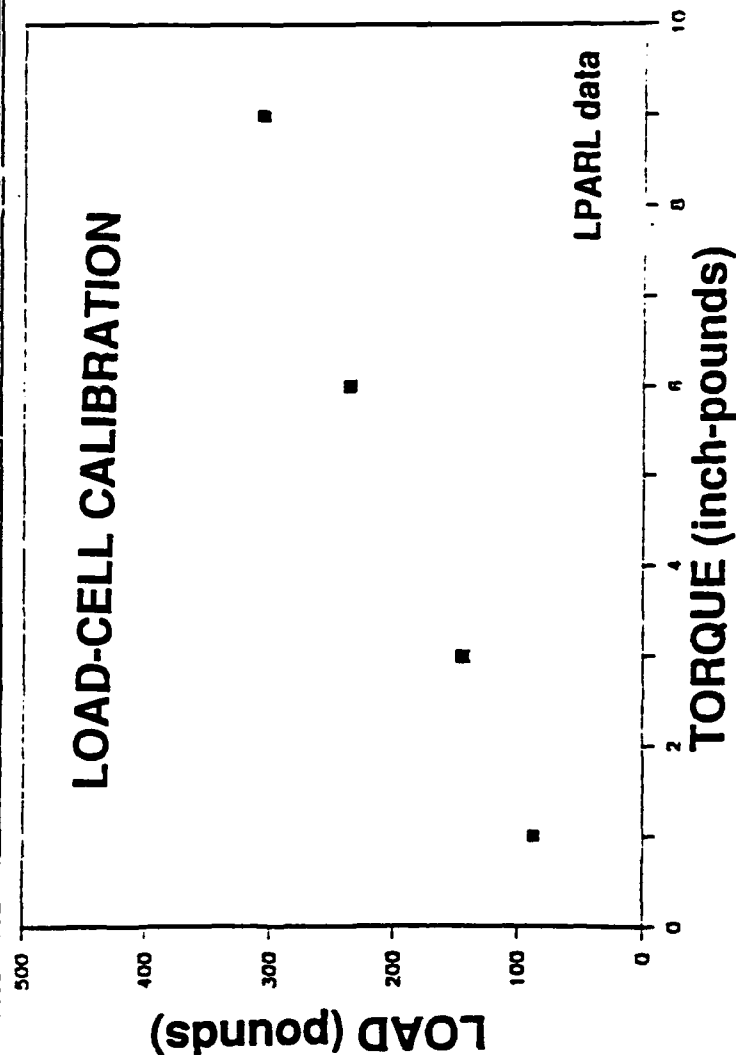
- Prepared for even distribution of Versicon over weld joint
- Preparation
 - Dissolved Nylon in trifluoroethanol at 130°C (high pressure)
 - Dispersed Versicon in Nylon/trifluoroethanol solution using ball mill
 - Free-standing films cast using doctor blade
 - Dispersion painted directly onto Nylon substrate
- Welding demonstrated with films in range from 90-950 ohms/square

II-B-149





ALL-PLASTIC PRESSURE RIG



II-B-150

- Designed for applying known pressure to samples during welding
- Does not heat up upon exposure to microwaves; made from Delrin
- Load applied by tightening plastic screws with torque wrench
- Linear response calibrated over range 20-100 psi
sample area is 3.4 square inches



PROGRAMMATIC STATUS

- Joe Zegarski became Principal Investigator at LPARL during Sept. 1991
 - Replaced Dr. Teh Kuan after he resigned
- Submitted two quarterly reports: 9-SEP-91, 31-DEC-91
- Presentations to:
 - Lockheed Corporate Composite Chairman Dr. Tak Aochi, 9-DEC-91
 - Lockheed Aeronautical System Company, Marietta, GA, 5-DEC-91
- Contributed to white paper submitted to Dr. Loda, Material Sciences Division, DARPA, 6-DEC-91



PLANS FOR REMAINING TIME ON SUBCONTRACT

- Obtain high-temperature polyaniline materials
- Weld PPS and PEEK using new polyanilines from Penn
 - Studies of pressure, time, & surface resistance effects
- Investigate curing and joining of thermosets
- Join thermoplastics and thermosets to metals using
 - conductive polymers
 - Induction or resistive-heating

REPORTS OF SUBCONTRACTORS

**TAKEN FROM
END-OF-YEAR REPORT
(JUNE 1, 1990 — MAY 31, 1991)**

University of Pennsylvania

Department of Materials Sciences & Engineering (Farrington)

End-of-Year Report (June 1, 1990 - May 31, 1991)

Brief Description of Project:

The goals of this program are to understand the structural characteristics of solid polymer electrolytes and their mechanism of ionic conductivity. These materials are of great commercial interest for use in high energy density batteries and electrochromic displays. Commercialization of this technology is currently underway in the United States (Ultracell, San Jose), the United Kingdom (Doughty Corp.), and Japan (Yuasa Battery Company) among others. Specific goals are as follows:

1. Understand the chemical and structural characteristics that lead to the formation of solid polymer electrolytes.
2. Characterize the ion/ion and ion/chain interactions that determine ion mobility and transport number in solid polymer electrolytes.

Significant Results During Last Year:

Solvation of Cobalt Salts by Oligomers Polyethers

Our approach to learning about the structural properties of solid electrolyte systems has involved the study of low molecular weight polyethers, such as poly(ethylene glycol), also known as PEG, as model systems.

The room temperature absolute viscosity of PEG-CoBr₂ solutions increases dramatically with salt content indicating that the complexation of Co(II) stiffens the oligomers chains, presumably due to a strong intermolecular "cross-linking" effect.

The PEG solutions exhibit maxima in conductivity at approximately 0.5M which is associated with the onset of a sharp increase in viscosity. This phenomenon can be attributed to the coupling of the mobility of the charged species with solution viscosity. Simply put, although increasing the salt concentration increases the number of charged species available to carry current, the solution viscosity increases as well, making macroscopic charge transport more difficult. The conductivity maximum indicates a balance between these two opposing forces: increasing numbers of charged species and decreasing carrier mobility.

Spectral deconvolutions indicate that in PEG at all concentrations studied (.02 - .75M) more than 50% of the cobalt present could be attributed to charged, octahedral species. The major tetrahedral species present is always ^{tet}CoBr₃L⁻ although ^{tet}CoBr₂L₂ is present in smaller amounts. At concentrations above .3M, the doubly charged ^{tet}CoBr₄²⁻ also becomes evident.

This work represents one of the first and certainly most complete resolutions of the structures of dissolved ions in a polymer electrolyte. As such, it stands as a basis for the effective 'calibration' of a variety of other techniques that have been used to explore structure in these materials.

Brief Summary of Plans for Next Years Work:

The principal goals for the coming year will be to complete the structure studies of PEO electrolytes using AXS and EXAFS and to expand studies of the local coordination of Co(II) ions in polymer electrolytes to longer chain polymers.

Montclair State College

Department of Chemistry (Humphrey)

End-of-Year Report (June 1, 1990 - May 31, 1991)

Brief Description of Project:

The primary goal of this project is to explore the possible uses of conducting polymers in biomedical applications. The first step in achieving this goal was to synthesize conducting polymers that could be used in such applications as electrochemical sensors, chromatography and dialysis. To accomplish this goal a host of novel conducting polymer/polysaccharide composite materials have been synthesized and patented. These materials have the physical properties of the polysaccharide matrix material and the optical/electronic properties of the conducting polymer, thereby making them ideally suited for use in the type of applications to be studied.

The second step of this project required the complete characterization of these composite materials, including spectroscopic analysis, electrochemical properties and conductivity measurements. The results of these investigations have acted as a guide to the use of these materials in the different proposed biomedical applications. For example, composites composed of a conducting polymer and microcrystalline cellulose is ideally tailored for unique chromatography applications, while conducting polymer/cellulose membrane composites are useful for sensor development and dialysis applications. Research into these applications, the last step in this project, has already begun.

Significant Results During Last Year:

During the past year significant progress has been made in the synthesis of new composite materials composed of polythiophenes and conventional polymers such as NAFION and GORE-TEX. Also, electrochemical sensors developed from polypyrrole/cellulose membrane composites have demonstrated voltage changes in response to solution concentrations of analyte molecules. However, the response is erratic and other configurations are being investigated. Finally, it has proved possible to "fine tune" the dialysis effect for conducting polymer/cellulose membrane composites through doping level of the conducting polymer. By adjusting the doping level the volume occupied by the conducting polymer in the molecular channels present in the cellulose membrane can be altered which adjusts the size of the molecular channels and marginally changes the dialysis characteristics of the membranes.

Brief Summary of Plans for Next Years Work:

Research during the coming year will focus on the further development of sensor technology expanding the present investigation by using amperometric methods in addition to the present used voltammetric methods. Also, reactions will be monitored which produce or use a dopant species, thus making it possible to follow the course of reaction by monitoring the conductivity of the composite material. In addition, any reaction which quantitatively converts analyte to a dopant species can be used in the indirect determination of the analyte using conducting polymer composite materials.

Further studies are also planned for the dialysis properties of composite materials and chromatography applications. During this year combination methods of chromatography/electrophoresis using the composite materials as the stationary phase in separation of mixtures of compounds having similar physical properties but different charges is planned. Such an investigation should demonstrate the superiority of using a combination method (chromatography/electrophoresis versus chromatography) in the separation of complex mixtures.

Drexel University

Department of Chemistry (Wei)

End-of-Year Report (June 1, 1990 - May 31, 1991)

Brief Description of Project:

The major objective of this project is to develop new synthetic methods for preparation of polyaniline and other conductive polymers with designed molecular weight and molecular weight distribution, and therefore to increase the electronic, thermal and mechanical properties of the polymers. The approach towards this goal includes development of a better understanding of the polymerization processes and evaluation/improvement of the key parameters of the thermal and mechanical properties of these polymers.

Significant Results During Last Year:

We have developed a new technology for preparation of electronic conductive polymers including polyaniline, polythiophene and polypyrrole, as resulted from our continuous effort in fundamental studies of the mechanism of Oxidative polymerization processes. This new technology offers many advantages over the existing ones. Using this new technology, the rate of polymerizations and the yield of the polymers are greatly increased by a factor of about 2 to 20; the properties of the resulting polymers, such as conductivity, uniformity of the polymer films, and adhesion of the films to the substrates, are improved. For example, the conductivity of poly(N-methylpyrrole) was improved by ca. 2 orders of magnitude. The new technology also offers a possible control of the polymer molecular weights and molecular weight distributions. The polymer structures can be tailored to obtain or further improve the properties such as processibility and mechanical strength. A new polymeric initiator based on polyacrylates was developed, upon which the conductive polymer chains grow to form a comb-like graft copolymer. The preliminary results show that the new materials have many interesting electronic, mechanical and thermal properties. We have also investigated acetylene-containing polymer systems with three-dimensionally conjugated backbones that could lead to a genuine intrinsic conductive polymer. We have also explored the application of the FAB and time-of-flight mass spectroscopy in the determination of the absolute molecular weights of polyaniline and its derivatives.

Brief Summary of Plans for Next Years Work:

We will continue the research and development of the new comb-like conductive polymers. In addition to the polyacrylate-based system, which has been successfully synthesized, we will investigate other polymer systems such as polystyrene, polyethylene, polyesters and polyamides. Thus, the electroactive polyaniline, polythiophene and polypyrrole chains will be grafted onto these conventional polymers in a controlled process with designed molecular weights. These new materials should have the good solubilities and thermal properties of the host polymers and the good electronic and optical properties of the conductive polymers.

University of Rhode Island

Department of Chemistry (Yang)

End-of-Year Report (June 1, 1990 - May 31, 1991)

Brief Description of Project:

The purpose of the research is to find a rational strategy for improving the electronic and optical properties of conducting polymers. In the period of 1987-89, we have used chemical modification and morphological modification to improve the properties of polyaniline. During the past year (1990-91) we have designed a technique to monitor the sub-forms and the heterogeneous sites of the conductive state of polyaniline. We have obtained spectroscopic and electrochemical signatures of these sub-forms or sites. We believe this information will lead to the understanding of "defects" in polyaniline and will lead to rational strategy towards making "defect-free" polyaniline.

Significant Results During Last Year:

The electrical or optical properties of conducting polymers (such as polyacetylene) have seen dramatic improvements by synthetic methods that greatly reduces "defects." These "defects" may be due to the lack of alignment of polymer chains, or the existence of conformational kinks, or short conjugation lengths. In the previous years we have devoted some efforts in examining the method of template-guided synthesis as a means to obtain polyaniline materials with more order and less defect. We have observed spectroscopic signatures of the morphologically improved samples. We also found that these spectroscopic details contain valuable information about various kinds of defects. These spectroscopic signatures of the "defects" may be a very useful handle for a systematic study of approaches to make "defect-free" conducting polymer materials.

During the past year we developed a new spectro-electrochemical technique that is capable of making much finer study of the structural transformation of polyaniline. Using this new technique, we discovered that there are several distinguishable forms of the conductive state of polyaniline. Our detailed spectro-electrochemical studies reveal spectroscopic and electrical signatures of these sub-forms. We think that these sub-forms represent different polymer conformations (or conjugated lengths) and different inter-chain interactions in a polyaniline sample with defects.

Brief Summary of Plans for Next Years Work:

We will concentrate on studying the factors that influence the existence of the sub-forms. We are interested in learning if the defects that limit the conjugation length are reflected in the co-existence of optically and electrochemically distinguishable sub-forms. If this is true, we will have a method for monitoring the defects while we attempt to use new synthetic methods to remove defects. The spectroscopic probe may be a useful tool for designing strategies for improving optical and electrical properties of polyaniline.

The purpose of this sub-contract is to construct a rational strategy for improving conducting polymers for applications in new electronic and optical devices.

Rensselaer Polytechnic Institute

Department of Chemistry (Wnek)

End-of-Year Report (June 1, 1990 - May 31, 1991)

Brief Description of Project:

The Binding of cationic polypeptides to polypyrrole [PP]/poly(styrenesulfonate)[PSS] and poly(N-methylpyrrole) [1NMP]/PSS films, along with the effect of binding on film electroactivity, have been studied using the electrochemical quartz crystal microbalance (EQCM). Our aim has been to demonstrate that the surface of conductive polymers films can be modified by protein adsorption. Two polypeptides were studied, namely poly(l-lysine hydro chloride) and the arginine-rich histone H3. This work was an inter-URI effort with Prof. John Reynolds of the University of Texas at Arlington.

Significant Results During Last Year: *

* No research was performed under no-cost extension period 6/1/90 - 12/31/90 because no funding was available. Dr. Wnek's subgroup was officially terminated from the DARPA grant on 12/31/90.

Brief Summary of Plans for Next Years Work:

NONE

REQUEST FOR FURTHER FUNDING FOR

**MICROWAVE
PROCESSING/WELDING/REPAIR
OF PLASTICS USING
CONDUCTING POLYMERS**

UNIVERSITY of PENNSYLVANIA

School of Arts and Sciences
Department of Chemistry
Chemistry Building
Philadelphia, PA 19104-6323

Tele: (215) 898-8307
(215) 898-9554
Home: (215) 623-6766
Fax: (215) 898-8378

December 6, 1991

Dr. Richard T. Loda
Program Manager - DARPA
Materials Science Division
3701 N. Fairfax Drive
Arlington, VA 22203-1714

VIA FAX: (703) 696-2201

Dear Rich:

Please find enclosed our summary of the use of conducting polymers in polymer processing which I mentioned in my Federal Express letter containing samples which you should have received today.

Microwave Processing/Welding/Repair of Plastics Using Conducting Polymers

Summary:

A method for the microwave processing/welding/repair of thermally processible plastics by the use of small quantities of a doped conducting polymer is described. The conducting polymer is either (i) painted or dusted onto the surfaces of massive pieces of plastic (thermoplastics or thermosets) which are to be welded together, or (ii) mixed with plastic powder which is to be consolidated into a unitary mass by melting, and is then exposed to microwave radiation, or (iii) mixed with the components of a thermoset plastic which requires elevated temperatures for curing. In each case non-conducting reinforcing fibers can be incorporated to form a composite. The heat evolved by the conducting polymer, when it absorbs and dissipates the microwave radiation, melts and fuses the plastic together. Conducting polymers are preferable to substances such as carbon black which can cause "hot

spots" which can decompose/deform the plastic. The conducting polymer can be appropriately chemically fine-tuned so as to "self-destruct" (chemically decompose) at a desired temperature just sufficient to cause melting of the plastic, thus avoiding the "hot spot" problem. Conducting polymers are also preferable to substances such as carbon black because of their better adhesion to the host polymer. The cost of the welding or curing process caused by the incorporation of the conducting polymer, polyaniline, is projected to be insignificant compared to the cost of the host polymer used.

Background:

Although the concept is in principle generally applicable to any conducting polymer, it has been demonstrated so far experimentally only with the conducting polymer, polyaniline (U.S. Patent allowed to A.J. Epstein, The Ohio State University). It stems directly from the Penn DARPA URI program and is a result of past and continuing collaborative research by the Lockheed, Ohio State, and Penn groups, the Ohio State and Lockheed work being funded by sub-contracts from the Penn DARPA URI contract. Continuing financial support of this program is sought.

Examples of Technological Use of Conducting Polymers in Polymer Processing

Examples of current technological problems which can be solved by the present approach include, but are not limited to:

- (i) Joining of sheets of plastic (0.25 - 0.5 inch thick and up to 4 - 8 feet in length/width) to form large and thick unitary laminated masses for aerospace uses (aircraft frame, fuselage, etc.), plastic submarine hulls (1 foot thick), etc. There is presently no good way known to fabricate such large structures. Such laminates are presently produced by heating the sheets so that they fuse together, but serious problems are encountered with "plastic flow" at the temperature needed for fusing, resulting in deformation of the structure.

A very real potential method for overcoming this problem comes from the Ohio State group which has shown that two pieces of polyethylene (m.p. 130°C) having a minute amount of conducting polyaniline between them can be welded together in a few seconds in a domestic microwave oven. A bond strength >50% that obtained by conventional methods results. Melting occurs only at the interface, the conducting polyaniline absorbing the microwave radiation and becoming hot.

This approach has recently been extended by the Lockheed group. Two blocks of Nylon 6,6 (1.5" x 2.0" x 0.75"), the interface between the blocks having been coated with a Versicon-Nylon 6,6 (m.p. 260°C) paint containing 45 mg of Versicon/inch² (Versicon is the Allied-Signal commercial conducting polymer, polyaniline). Application of a pressure of 20 lbs/inch² and exposure in a domestic microwave oven for 20 seconds resulted in a very strong 1500 psi tensile strength bond line. A specimen was sent to Dr. Richard T. Loda by Federal Express on Thursday, December 5, 1991. It should be noted that excellent seals can now be obtained using only 10 mg of Versicon/inch². It can be seen from the submitted sample that there is no weld deformation — for example, the edges of the sample are still sharp. Welding of the thermoplastic pieces occurs with no heating or deformation of the bulk thermoplastic. A method of applying the conducting polymer (Versicon) to the surface to be welded is demonstrated in the case of Nylon 6,6 (Sample sent to Dr. Richard T. Loda on December 5, 1991) in which a "paint" consisting of a mixture of Nylon 6,6 and Versicon has been coated on one of the surfaces to be bonded.

For the microwave-induced processing of composites, electrically conductive polymers have several advantages over competitive materials such as metals, graphite, or inorganic semiconductors. Upon exposure to microwave radiation, a material that is too conductive will cause undesirable electrical arcing and "hot spots" deleterious to the plastic. They also present a possible fire hazard because of rapid overheating. A material that is too resistive will heat too slowly for practical application. It is well established that a conductive polymer such as polyaniline can be doped to any desirable

level in the $\approx 10^{-6}$ to 10^2 S/cm range. Other overall technical advantages stem from the versatility of conductive polymers, i.e., the ability to create a conductive polymer having the appropriate combination of microwave response and thermal stability.

Another important advantage of a conducting polymer is that its coefficient of thermal expansion is more closely matched to that of thermoplastics than are those of the competitive materials. This will lead to weld joints having greater strength and better long-term aging behavior, especially in aerospace applications, which frequently have environments with large temperature cycles. Previous work at Lockheed on this URI project has used the basic principle of "like dissolves like" by chemically grafting oligomers of the host plastic on to the polyaniline chain to increase its compatibility and adherence to the host polymer. This is a very important feature of this system.

Perhaps the most important advantage of polyaniline is that its thermal stability can be tuned to desired levels with the use of different dopants. This feature is critical to prevent thermal runaway "hot spots" arcing, etc. in a welding system. Once the polyaniline reaches its decomposition (undoping) temperature, it will become nonconductive. Further exposure to microwave radiation will, therefore, not cause heating of the undoped polyaniline. Thus, in microwave-induced processing of composites, polyaniline is a self-regulating heating material.

(ii) Similar arguments to those given in (i) above can also be applied to thermoplastics reinforced with nonconducting fibers made from glass, boron, Kevlar, or new fibers made from poly(benzoxazole) being developed by Dow Chemical Company having good mechanical properties. The use of conducting polyaniline fibers (Penn patent resulting from the Penn DARPA URI program) now being fabricated by spinning techniques at DuPont, opens up a potentially very important large new area of conducting composites.

(iii) The advantages of the above method are also applicable to thermoset systems which require elevated temperatures for curing. Thermoset systems which have the potential of being mixed with small quantities of conducting

polymers and then cured by microwave radiation include unsaturated polyesters, vinyl ester, allyl-monomer, bismaleimide resins using organic peroxide as catalyst, and acetylene-terminated polyimides.

Applications include, for example, the stacking of reinforced-thermoset laminates. If small amounts of polyaniline were mixed with the components before using and exposed to microwave radiation, heating would occur on the outside and would cease when desired temperature was reached due to the thermal decomposition of the polyaniline. The radiation would then go in further into the thermoset, heat the thermoset and then decompose. A "wave" of heat would thus travel through the thermoset mass from one side to the other.

(iv) The above concepts are also ideally suited to the repair of thermoset composite structures. The application of field repair is very important to defense-related composites. Field repair refers to the fixing of battle-damaged composite structures in a battle-field situation. This is an enormous problem to experts concerned with composites. It appears that the solution may lie in conducting polymers.

Notes:

- (1) Although the term "microwave radiation" has been used throughout, this actually includes other types of electromagnetic radiation including induction heating and R.F., etc.
- (2) The cost of the Versicon involved in the above process is insignificant based on the cost of aerospace plastic of ~\$90/lb(?). The present cost of Allied-Signal's Versicon conducting polyaniline is \$180/lb. which will drop to \$35/lb. when under full production. This latter price results in a polyaniline cost of \$70 for a 25 ft. x 25 ft. ($\$0.11/\text{ft.}^2$) laminate based on ~10 mg of Versicon/inch². Since the weight of a 25 ft. x 25 ft. x 0.5 inch piece of polymer is ~1 ton, it is clearly apparent that the cost of the conducting polymer component is negligible.

- (3) DARPA is now funding a multimillion dollar project at Lockheed Palo Alto Research Laboratories (LPARL) for building a composite part of the flight deck for a composite-hull submarine. The above approach seems well-suited for submarine hull, etc. applications.
- (4) The Penn group has made significant recent advances in increasing the decomposition temperature of polyaniline by the incorporation of polyhedralborohydride anions and inorganic polymetaphosphate anions. Appropriate chemical modification of the dopant should result in a wide range of decomposition temperatures suited for different types of thermoplastic or thermoset resins. Considerable work has also been done in derivatization of polyanilines resulting in greater compatibility with host polymers.

Proposed Program:

We propose a closely-knit and coordinated academic/industrial interdisciplinary program involving Ohio State University, Penn and Lockheed to determine chemical composition/structure/mechanical/stability/electromagnetic response/relationships in conducting polymers, particularly polyanilines such as those studied at Penn and Ohio State University and those commercially available from Allied-Signal and Hexcel. These properties will be appropriately exploited for the development of technologically useful processing of thermoplastic, thermoset resins and their composites.

Should you require further information please do not hesitate to let me know.

Sincerely yours,



Alan G. MacDiarmid
Blanchard Professor of Chemistry

AGM/mam

cc: Dr. Arthur J. Epstein
Mr. Joseph Zegarski
Dr. Joanne Milliken
Dr. Kenneth J. Wynne

APPENDIX

A

PRE- AND POST-DOCTORAL FELLOWS

EMPLOYED FROM

4/1/90 TO 9/30/91

UNIVERSITY RESEARCH INITIATIVE PROGRAM
UNIVERSITY OF PENNSYLVANIA

Pre- & Post-Doctoral Fellows Employed
4/1/90 — 9/30/91

Name	Institution	Starting Date	Ending Date	FTE	Subsequent Employment
------	-------------	---------------	-------------	-----	-----------------------

Post Doctoral Fellows

R. Bakthavatchalam	Drexel	10/1/89	Present	0.25*	Continuing
D.C. Yang	Drexel	10/1/89	Present	1.00	Continuing
					* Non-salary research supplies
John L. Isidor	Montclair	6/1/91	9/1/91	1.00	Montclair State
John M. Ginder	OSU	7/1/88	10/5/90	1.00	Ford Research Labs, Michigan
Joanna Wiesinger	U of Penn	9/15/91	Present	1.00	Continuing
Woan-Ru Shieh	U of RI	1/1/90	Present	1.00	Continuing

Graduate Students

R. Allenbach	Drexel	9/1/90	Present	0.50*	Continuing
C.-C. Chan	Drexel	10/1/89	5/31/90	0.25*	ISI
A. Chan	Drexel	9/1/90	Present	0.50*	Continuing
C.G. Clark	Drexel	9/1/90	4/1/91	0.25*	Drexel Univ.
E. Connors	Drexel	9/1/88	11/30/90	0.25*	Betz Lab
R. Hariharan	Drexel	9/1/87	Present	0.50*	Continuing
K.F. Hsueh	Drexel	9/1/87	Present	0.50*	Proctor & Gamble
J. Tian	Drexel	9/1/89	Present	0.25*	Continuing
C. Whitecar	Drexel	9/1/88	5/31/90	0.25*	ISI
					* Non-salary research supplies
Kimberly Coplin	OSU	1/1/91	Present	1.00	Continuing
Keith Cromack	OSU	9/15/86	Present	1.00	Continuing
Gang Du	OSU	7/1/90	Present	1.00	Supported by AFOSR
-	OSU	7/1/90	8/31/91	1.00	Supported by DOE, NEDO
Mikolaj Jozefowicz	OSU	10/1/89	Present	1.00	Continuing
Kwangjoon Kim	OSU	1/1/89	Present	1.00	Continuing
Jingmin Leng	OSU	4/25/88	Present	1.00	Continuing
Stephen Long	OSU	4/1/90	Present	1.00	Continuing
Zhaohui Wang	OSU	7/1/88	9/30/91	1.00	Post-Doc (MIT)
Jiang Yue	OSU	10/1/89	9/30/91	1.00	Post-Doc (MIT)
Robert Clark	U of RI	5/10/87	Present	1.00	Continuing
Richard Cushman	U of RI	9/15/86	8/29/87	1.00	Leave of Absence, 1 year
Brian Schmitz	U of RI	5/10/87	12/30/88	1.00	Graduate Studies

Sanjeev Manohar	U of Penn	1/1/90	Present	1.00	Continuing
James Masters	U of Penn	5/1/88	Present	1.00	Continuing
Elliot Scherr	U of Penn	6/1/87	Present	1.00	Continuing
David Swanson	U of Penn	7/1/87	Present	1.00	on NSF Support
Yan Sun	U of Penn	7/1/88	9/91	*	Rohm & Hass

* Received 68% from 7/90 to 12/90 and
received 100% from 1/91 to 9/91.

Xun Tang	U of Penn	7/1/88	8/91	*	Rohm & Hass
----------	-----------	--------	------	---	-------------

* Received 68% from 7/90 to 12/90.

Heng Cai	U of Penn	9/1/90	Present		Continuing
Gregory Jones	U of Penn	4/1/90	1/31/91		
Bruce Katz	U of Penn	9/1/91	Present		Continuing
Michael Mendolia	U of Penn	9/1/91	Present		Continuing
Jun Xu	U of Penn	9/1/90	Present		Continuing

Undergraduate Students

D. Glahn	Drexel	1/2/91	Present	0.50*	Continuing
----------	--------	--------	---------	-------	------------

John Berezny	Montclair	10/1/88	6/1/90	0.50	Student
Alex Kozak	Montclair	10/1/88	6/1/90	0.50	Student
Nancy Moran	Montclair	10/1/88	6/1/90	0.50	Student
Rich Pucci	Montclair	10/1/88	6/1/90	0.50	Student
Kwynne Pugh	Montclair	6/1/91	Present	0.10*	Continuing

* No stipend paid

Kim Crawford	OSU	12/17/90	1/11/91	0.50	Univ. of Tennessee
Aaron Freimark	OSU	5/25/90	8/31/90	0.50	Cornell Univ.
Greg Gordon	OSU	11/5/90	Present	0.50	Continuing
Kelly Kutscherenko	OSU	3/1/90	6/30/90	0.50	Student
Livia Oh	OSU	6/8/90	Present	0.50	Continuing
Eugene Reyzer	OSU	6/25/90	9/30/90	0.50	Cal Tech Univ.

Visiting Scientist

L.G. Tang	Drexel	9/1/91	Present	0.20	Continuing
-----------	--------	--------	---------	------	------------

Angelica Fagot	U of Penn	9/1/91	Present	1.00	Continuing
----------------	-----------	--------	---------	------	------------

Work Study

Mark Bauer	U of Penn	7/90	12/90	0.20	Dupont
------------	-----------	------	-------	------	--------

APPENDIX

B

INDUSTRIAL & ACADEMIC INTERACTIONS

INDUSTRIAL & ACADEMIC INTERACTIONS *

* The following interactions between personnel funded by the URI contract/grant have taken place during this time period (4/1/90 - 9/30/91), including:

- Joint research meetings of two or more groups
- Exchange visits involving one or more group members
- Numerous telephone and facsimile interactions (very frequently directly between students and/or non-supervisory personnel)

May 9-11, 1990, Drs. MacDiarmid, Epstein, and members of their group met at Somerset, PA to discuss ongoing collaborative research. Members of Dr. MacDiarmid's group who attended were: G. Asturias, S. Manohar, J. Masters, E. Scherr, D. Swanson, X. Tang, Y. Sun, H. Weiss, Dr. G.W. Jang and Dr. R.K. Kohli. Members of Dr. Epstein's group who attended were: M. Józefowicz, K. Kim, J. Long, G. Du, Z. Wang, J. Yue, K. Cromack, K. Coplin, Dr. J.M. Ginder and Dr. R. McCall.

May 29-31, 1990, Dr. T. Kuan (Lockheed) had several technical discussions with Professor MacDiarmid and Professor Epstein during his invited talk at the European Physical Society - Industry Workshop, at Lofthus, Norway.

June 13-14, 1990, Dr. Epstein visited Dr. MacDiarmid's office for discussing ongoing research projects and for the forthcoming DARPA-Polymer Review at Arlington, VA.

June 21, 1990, Dr. T. Kuan (Lockheed) had extensive discussions with Mr. S. Manohar of the University of Pennsylvania, and Professor Epstein of Ohio State University in preparation for the joint presentation at the DARPA Polymer Program Review at Arlington, VA.

June 21-22, 1990, Drs. MacDiarmid, Epstein and McCall met with DOD officials and other collaborators/subcontractors at the last DARPA Review Meeting in Washington D.C.

August 8, 1990, Dr. Epstein visited Dr. MacDiarmid's office to discuss collaborative research.

September 2-7, 1990, Interactions between several members of the Ohio State and University of Pennsylvania research groups occurred at the International Conference on Synthetic Metals in Tübingen, Germany.

October 15-16, 1990, Dr. Epstein met with Dr. MacDiarmid at Penn to discuss polymer research.

October 31-November 1, 1990, Drs. MacDiarmid and McCall met with officials at Wrightsville Beach, North Carolina for a program review.

November 28, 1990, Dr. Epstein met with Professor William Doane of the Liquid Crystal Institute at Kent State University, Kent, Ohio, to discuss current polymer research.

March 18-22, 1991, Drs. MacDiarmid, Epstein, and members of their research groups met several times during the 1991 March Meeting of the American Physical Society in Cincinnati, Ohio.

April 16-19, 1991, Drs. MacDiarmid and Epstein met during the ACS 1991 National Meeting in Atlanta, Georgia, to discuss collaborative research.

May 6-7, 1991, Drs. MacDiarmid and Epstein met during the 49th Annual Technical Conference of the Society of Plastics Engineers in Montreal, Canada, to discuss collaborative research.

June 12-18, 1991, Drs. MacDiarmid and Epstein attended the Nobel Symposium #NS-81 "Conjugated Polymers and Related Materials: The Interconnection of Chemical and Electronic Structure," in Lulea, Sweden, to discuss collaborative research.

August 27, 1991 - URI subcontractor from Lockheed Corporation visited Dr. MacDiarmid's laboratory to discuss the future directions of research for this URI funded program. The following people from Lockheed attended: Dr. James F. Wolfe, Dr. Robert H. Boschan and Mr. Joseph Zegarski. in addition, Dr. A.J. Epstein of Ohio State University also attended this meeting.

APPENDIX

C

INVITED PRESENTATIONS

INVITED PRESENTATIONS *

* The following presentations and interactions funded by the URI contract/grant have taken place during this time period (4/1/90 – 9/30/91), including:

- Lectures on research at organized symposia.
- Visits to laboratories by persons concerned with conducting polymers & any subsequent talks/seminars/etc.
- Visits by subcontractors to other laboratories & any subsequent talks/seminars/etc.

April, 1990 — Dr. Y. Wei visited George Washington University, Washington, D.C. Title of invited talk given by Dr. Wei, "Chemistry of Electrically Conductive Polymers."

April, 1990 — Dr. Y. Wei, along with C.C. Chan, J. Tian and G.W. Jang, attended the DE/Philadelphia Section of SAMPE, Philadelphia, PA. Third prize winner for the talk given titled, "Novel Synthesis of Polythiophenes."

April, 1990 — Dr. Y. Wei, along with C.C. Chan, J. Tian and G.W. Jang, attended the Sigma Xi Sci. Res. Symp., Philadelphia, PA. Title of the invited talk given, "Synthesis and Electrical Properties of Polythiophene and Its Derivatives."

April, 1990 — Dr. G.C. Farrington attended the 48th Frontiers in Chemistry Lecture Series at Case Western Reserve University, Cleveland, Ohio. Title of invited talk given by Dr. Farrington, "Fast Ionic Transport in Solid State Batteries to Laser."

April 20, 1990 — Research Specialist Dr. Barbara F. Howell and Post-Doctoral Fellow Thomas Diberardino, from David Taylor Ship Research and Development Center, visited Dr. MacDiarmid's office to discuss Schiff base condensation type of products for radar application using conducting polymers.

April 30, 1990 — Professor Eugene Mele, from the University of Pennsylvania, visited Dr. Epstein's laboratory. Title of invited talk given by Professor Mele, "Parastatistics in the Strongly Correlated Two-Dimensional Hubbard Model."

May 18, 1990 — In conjunction with University of Pennsylvania's 250th Anniversary Celebration, Dr. MacDiarmid participated in a faculty exchange program entitled, "New Materials for a New Century."

May 21-24, 1990 — Dr. T. Kuan along with Deanne P. Yamato and Sandra K. Clement attended the Advanced Aerospace Materials/Processes Conference, Long Beach, California. Title of the invited talk given by Dr. T. Kuan, "Thermosetting Conductive Polyaniline/Polimide Blends."

May 24-27, 1990 — Dr. Epstein visited Professor Jean-Paul Pouget at the Universite Paris-Sud, Orsay, France, to discuss structure studies of polyaniline.

May 28-31, 1990 — Dr. MacDiarmid attended European Physical Society (EPS) Meeting at Loftus, Norway. Title of the invited talk given by Dr. MacDiarmid, "The Polyanilines: Potential Technology Based on New Chemistry and New Properties."

- May 28-31, 1990 — Dr. Epstein attended Europhysics Industrial Workshop on the Science and Applications of Conducting Polymers, in Loftus, Norway. Title of the invited talk given by Dr. MacDiarmid, "The Controlled Electromagnetic Response of Polyanilines and Its Applications to Technologies."
- May 29-31, 1990 — Dr. T. Kuan attended the European Physical Society meeting at Loftus, Norway. Title of the invited talk given by Dr. T. Kuan, "Electrically Conductive Polymers for the Aerospace Industry."
- June 1-2, 1990 — Dr. MacDiarmid visited Trondheim University in Sweden. Title of the invited talk given by Dr. MacDiarmid, "Polyaniline: Chemical and Physical Basis for its Applicability as an Electroactive Material."
- June 5-6, 1990 — Dr. MacDiarmid received honorary doctorate degree from Linköping University, Sweden. Title of the invited talk given by Dr. MacDiarmid at the University, "Synthetic Metals: A Novel Role for Organic Polymers," and also another talk at the Department of Physics and Measurements, "Polyaniline: Chemical and Physical Basis for its Processibility."
- June 6-9, 1990 — Graduate student (of Dr. A.G. MacDiarmid's group) Elliot Scherr made a visit to Foster-Millar Corporation, Boston, MA, to do collaborative research on the stretch-alignment of polyaniline films.
- June 12, 1990 — Professor Sumit Mazumdar, from the University of Arizona, visited Dr. Epstein's laboratory. Title of invited talk given by Dr. Mazumdar, "Interlacing Electrons in Reduced Dimensions."
- June 12-14, 1990 — Drs. S. Preto-Clement and R.E. Cameron visited the 4th International SAMPE Electronic Materials and Processes Conference, Albuquerque, New Mexico. Title of the contributed talk given by S. Preto-Clement and R.E. Cameron, "Oxidative Polymerization of Aniline: Characterization of New Polyaniline Products."
- June 14, 1990 — Dr. Epstein visited Dupont, in Wilmington, Delaware, to discuss joint research on polymer fibers.
- June 20 - July 12, 1990 — At the invitation of the Japan Society for Promotion of Science (J.S.P.S.) Dr. MacDiarmid visited several universities and industries in Japan. Title of the invited talk given by Dr. MacDiarmid at the universities, "Polyaniline: Chemical and Physical Basis for its Application as an Electroactive Material." The title of the invited talk given at the industries, "Polyanilines: Potential Technology Based on New Chemistry and New Physics."
- June 21-22, 1990 — DARPA held URI program review at Arlington, VA. Sanjeev Manohar, a graduate student of Dr. MacDiarmid's, along with Drs. Epstein and Kuan attended the conference and presented the invited talk entitled, "Polymers by Non-Redox Processes: Synthesis, Physical Studies and Application." Others who attended the talks were Drs. Rich McCall (OSU), Yen Wei (Drexel U.) and Sze Yang (U. of Rhode Island).
- June 27, 1990 — Dr. Geoffrey A. Lindsay, from the Naval Weapons Center, China Lake, California, visited Dr. Epstein's laboratory. Title of invited talk given by Dr. Lindsay, "Second Order Nonlinear Optical Polymers."

- June 28, 1990 — Dr. Gordon Yee, from DuPont, visited Dr. Epstein's laboratory. Title of invited talk given by Dr. Lee, "Determination of the Symmetry of the Pair Function in Superconducting YBCO."
- July 10, 1990 — Professor Dan Davidov, from the Hebrew University in Jerusalem, visited Dr. Epstein's laboratory. Title of invited talk given by Professor Davidov, "Electrical, Magnetic, and Optical Properties of Conjugated Ladder Polymers."
- July 23, 1990 — Dr. R. Gregory, Department of Textiles and Polymer Science, Clemson University, Virginia visited Dr. MacDiarmid's laboratory to discuss research on conducting polymers.
- July 27, 1990 — Dr. S. Miyata, Department of Materials Science and Engineering, Tokyo University of Agriculture and Technology, Tokyo, Japan, visited Dr. MacDiarmid's laboratory. Title of the invited talk given by Dr. Miyata, "Chemical Polymerization of Pyrrole."
- August 1-3, 1990 — Dr. MacDiarmid attended Gordon Conferences on "Electronic Processes in Organic Materials" at Plymouth, New Hampshire. Title of the invited talk given by Dr. MacDiarmid, "Polyaniline: Chemical and Physical Basis for its Processability."
- August 14-16, 1990 — Professor Mitsuo Ishikawa of Hiroshima University, Japan visited Dr. MacDiarmid's laboratory. Title of the invited talk given by Prof. Ishikawa, "Synthesis and Conducting Properties of Poly[(disilanylene)butenes] and Poly[(disilanylene)ethynylenes]."
- August 16, 1990 — Prof. Adam Pron of the University of Warsaw Poland visited Dr. MacDiarmid's laboratory. Title of the invited talk given by Prof. Pron, "Synthesis and Characterization of Highly Stereoregular Poly 4-4' diakly-2-2' bithiophenes."
- August 22-23, 1990 — Dr. Y. Furukawa, Department of Chemistry, University of Tokyo, Japan visited Dr. MacDiarmid's Laboratory. Title of the invited talk given by Dr. Furukawa, "Detection of Polarons and Bipolarons in Conducting Polymers by Raman Spectroscopy."
- August 26-31, 1990 — Mr. Jiang Yue attended the 200th Meeting of the American Chemical Society, in Washington D.C. Title of invited talk given by Mr. Yue, "Synthesis of Aqueous Soluble, Self-Doped Conducting Polyaniline."
- August 28-30, 1990 — Dr. MacDiarmid visited Prof. H. Naumann's laboratory at BASF, Ludwigshafen, FRG. Title of the invited talk given by Dr. MacDiarmid, "The Polyanilines: Potential Technology Based on New Chemistry and New Properties."
- September 2-7, 1990 — Dr. MacDiarmid and other members of his group attended the ICSM Conference at Tübingen, West Germany. The following members attended; Graduate students Mr. Sanjeev Manohar, Jim Masters, Elliot Scherr, Dave Swanson and Gabriel Asturias (support from other sources) and Dr. Rakesh K. Kohli (support from other sources). Title of the invited talk given by Dr. MacDiarmid, "Pernilgraniline: Synthesis and Properties." The following posters were also presented:
- "Impedance Profiling: A Convenient Technique for Determining the Redox or Protonic Acid Doping Characteristics of Conducting Polymers," D.B. Swanson, A.G. MacDiarmid and A.J. Epstein.

"Polyaniline: Permitted Oxidation States," J.G. Masters, Y. Sun, A.G. MacDiarmid and A.J. Epstein.

"Polyaniline: Pernigraniline, An Isolable Intermediate in the Conventional Chemical Synthesis of Emeraldine," S.K. Manohar, A.G. MacDiarmid and A.J. Epstein.

"Polyaniline: Oriented Films and Fibers," E.M. Scherr, A.G. MacDiarmid, S.K. Manohar, J.G. Masters, Y. Sun, X. Tang, M.A. Druy, P.J. Glatkowski, K.R. Cromack, M.E. Jozefowicz, J.M. Ginder, R.P. McCall and A.J. Epstein.

"The Electronic Structure of Processable Emeraldine As Studied by Photoelectron Microscopy," P. Dannetum, M. Logdlund, R. Lazzaroni, S. Stafstrom, W.R. Salaneck, E. Scherr and A.G. MacDiarmid.

"The Evolution of the Electronic Structure of Polyacetylene, Poly(P-phenylene) and the Copolymer Poly(P-phenylene vinylene) As Studied by Photoelectron Spectroscopy," M. Logdlund, W.R. Salaneck, S. Stafstrom, D.D.C. Bradley, R.H. Friend, K.E. Ziemelis, G. Froyer, D. Swanson, A.G. MacDiarmid and J.L. Bredas.

Titles of the invited talks given by Dr. Epstein's group, "Excitation and 'Metallic' State in Polyaniline and its Derivatives," A.J. Epstein and A.G. MacDiarmid; "Structure, Order, and the Metallic State in Polyaniline and Its Derivatives," A.J. Epstein and A.G. MacDiarmid; and "Ring Torsional Polarons in Polyaniline and Polyparaphenylene Sulfide," J.M. Ginder and A.J. Epstein. The following posters were also presented:

"Photoinduced Electron Spin Resonance in Polyaniline Polymers," K.R. Cromack, J.G. Masters, Y. Sun, A.J. Epstein and A.G. MacDiarmid.

"Photoexcitation Spectroscopy of Pernigraniline," J.M. Leng, J.M. Ginder, R.P. McCall, H.J. Ye, A.J. Epstein, Y. Sun, S.K. Manohar and A.G. MacDiarmid.

"Photoinduced Absorption and Erasable Optical Information Storage in Polyanilines," R.P. McCall, J.M. Ginder, J.M. Leng, H.J. Ye, A.J. Epstein, G.E. Asturias, S.K. Manohar, J.G. Masters, E.M. Scherr, Y. Sun and A.G. MacDiarmid.

"X-ray Structure of Polyanilines," J.P. Pouget, M.E. Jozefowicz, A.J. Epstein, J.G. Masters, A. Ray, Y. Sun, X. Tang and A.G. MacDiarmid.

"Electron Localization in Polyaniline Derivatives," Z.H. Wang, A.J. Epstein, A. Ray and A.G. MacDiarmid.

"Sulfonic Acid Ring-Substituted Polyaniline, A Self-Doped Conducting Polymer," J. Yue, Z.H. Wang, K.R. Cromack, A.J. Epstein and A.G. MacDiarmid.

"Thermal Stabilities of Polyaniline," J. Yue, A.J. Epstein, Z. Zhang, P.K. Gallagher and A.G. MacDiarmid.

"Polyaniline/PPD-T Fibers," C.H. Hsu, P. Vaca-Segonds and A.J. Epstein.

September 9-14, 1990 — Dr. Epstein visited Professor Jean-Paul Pouget at the Universite Paris-Sud, Orsay, France, to discuss structure studies of polyaniline.

- September 24 - October 8, 1990 — Mikolaj Jozefowicz performed x-ray diffraction experiments on polyaniline at the Universite Paris-Sud, Orsay, France, in collaboration with Professor Jean-Paul Pouget.
- September 25, 1990 — Xun Tang and Sanjeev Manohar of Dr. MacDiarmid's group collaborated with Dr. Che Hsu of Dupont Experimental Station, Delaware, to conduct studies on molecular weight determination of emeraldine base, using light scattering devices. These will then be compared with molecular weight determined by GPC. Same experiments were also carried on 9/27/90.
- September 26, 1990 — Mr. Sanjeev Manohar and Dr. MacDiarmid attended the Philadelphia Section of the Electrochemical Society meeting at the University of Pennsylvania, Philadelphia. Title of the invited talk given by Mr. Manohar, "Polyaniline: Electrochemistry and Application to Rechargeable Batteries."
- October 2, 1990 — Mr. Sanjeev Manohar, a graduate student from Dr. MacDiarmid's group, performed some collaborative experiments with Dr. Che Hsu of Dupont Experimental Station, Delaware, on water soluble polyaniline solutions and films.
- October 2-3, 1990 — Dr. Epstein visited DuPont, in Wilmington, Delaware, to discuss joint polymer research.
- October 3, 1990 — Dr. Yen Wei visited the Delaware Valley Thermal Analysis Forum, Philadelphia, PA. Title of invited talk given by Dr. Wei, "Thermal Characterization of Electrically Conductive Polymers."
- October 15, 1990 - November 1, 1991 — Dr. B.V.R. Chowdari, Professor of Physics, University of Singapore, visits Dr. Farrington's department & laboratory as a visiting scientist.
- October 15-16, 1990 — Drs. MacDiarmid and Epstein met at Allied-Signal, in Morristown, New Jersey, to discuss polymer research efforts with Drs. Ray Baughman, Ron Elsenbaumer, and Larry Shacklette.
- October 19-20, 1990 — Dr. Richard McCall, Kim Coplan, Keith Cromack, Mikolaj Jozefowicz and Kwangjoon Kim attended the Symposium on Ultrafast Spectroscopy and High Resolution Spectroscopy at The Ohio State University.
- October 22, 1990 — Drs. Epstein and McCall met with Professor Sam Jeneke, from the University of Rochester, and Drs. Charles Lee, Ted Helminiak, Bob Spry and Fred Arnold at Wright Patterson Air Force Base in Dayton, Ohio, to discuss joint research on Conducting polymers and ladder polymers.
- October 25, 1990 — Dr. Francis Garnier, C.N.R.S., France, visited Dr. MacDiarmid's laboratory. Title of invited talk given by Dr. Garnier, "Organic Conjugated Semiconductors."
- October 26-27, 1990 — Dr. Epstein visited Professor Jean-Paul Pouget at the Universite Paris-Sud, Orsay, France, to discuss structure studies of polyaniline. (Not funded by DARPA.)
- October 28 - November 2, 1990 — Dr. Epstein attended the NATO Advanced Research Workshop on Magnetic Molecular Weight Materials in Il Ciocco, Italy. Title of invited talk given by Dr. Epstein, "Physics of the 1-D Molecular Ferromagnet Decamethylferrocenium Tetracyanoethanide, [DMeFc] + [TCNE]-." (Not funded by DARPA.)

- October 30 - November 1, 1990 — Dr. MacDiarmid attended DARPA meeting Wrightsville, North Carolina. Title of the invited talk given by Dr. MacDiarmid, "Polymers By Non-Redox Processes: Synthesis, Physical Studies and Application."
- November 7-9, 1990 — Dr. MacDiarmid attended IUPAC International Symposium on Speciality Polymers at Singapore. Title of the invited talk given by Dr. MacDiarmid, "Synthetic Metals: A Novel Role for Organic Polymers."
- November 7-9, 1990 — Dr. Epstein attended IUPAC International Symposium on Speciality Polymers at Singapore. Title of the invited talk given by Dr. Epstein, "Novel Concepts in Electronic Polymers: Polyaniline and Its Related Ring-Containing Polymer Systems."
- November 16, 1990 — Dr. MacDiarmid visited University of South Carolina at Columbia. Title of the invited talk given by Dr. MacDiarmid, "Synthetic Metals: A Novel Role for Organic Polymers."
- November 16, 1990 — Dr. Sze Cheng Yang attended the Symposium on Electrochromic Devices in the annual meeting of the American Institute of Chemical Engineers, Chicago, Illinois. Title of the invited talk given by Dr. Yang, "Molecular Engineering of Polyaniline for Electrochromic Applications."
- November 18-20, 1990 — Dr. MacDiarmid attended 15th Biennial Polymer Symposium at Ft. Lauderdale, Florida. Title of the invited talk given by Dr. MacDiarmid, "Polyaniline: New Chemistry Oriented Films and Fibers."
- November 28, 1990 — Dr. Epstein attended Professor William Doane's laboratory at the Liquid Crystal Institute, Kent State University to discuss polymer research. Title of invited talk given by Dr. Epstein, "Ring Around a Polymer: New Physics in Polyaniline."
- November 29, 1990 — Professor Ken Singer of Case Western Reserve University visited Dr. Epstein's laboratory. Title of invited talk given by Professor Singer, "Non-Linear Optical Properties of Conjugated Polymers."
- December 4, 1990 — Dr. Alan Bishop of Los Alamos National Lab visited Dr. Epstein's office to discuss current polymer research.
- December 11, 1990 — Drs. Y. Matsuyama and Y. Kato of Tyobo New York, Inc., visited Dr. MacDiarmid's laboratory for discussions on conducting polymers.
- December 12, 1990 — Dr. Shigenori Otsuka of Mitsubishi Kasei America, Inc., visited Dr. MacDiarmid's office. Title of the invited talk given by Dr. Otsuka, "The Extrinsic Photocarrier Generation Process In The Double Layer Organic Photoconductor."
- December 17-18, 1990 — Professor Howard Reiss of Department of Chemistry, UCLA, Los Angeles, California, visited Dr. MacDiarmid's laboratory. Title of the invited talk given by Dr. Reiss, "Donnan Potential."
- January 9-11, 1991 — Professor Steven Kivelson of UCLA visited Dr. Epstein's laboratory, discussing current research in organic conductors. Title of invited talk given by Professor Kivelson, "Scaling Theory of Competing Electron-Electron and Electron-Lattice Interactions in 1-D: Metal-Nonmetal Transition in Polyacetylene."

- February 1, 1991 — Dr. Michael Rice of Xerox-Webster Research Center visited Dr. Epstein's laboratory, discussing current experimental and theoretical results on conducting polymers. Title of invited seminar given by Dr. Rice, "Concepts in Conducting Polymers."
- February 4, 1991 — Dr. Clifford N. Matthews of University of Illinois at Chicago, visited Dr. MacDiarmid's laboratory. Title of the invited talk given by Dr. Matthews, "Cosmochemistry and the Origin of Life."
- February 4, 1991 — Dr. Kumar Patel of AT&T Bell Laboratories visited Dr. Epstein's laboratory, discussing current research in materials science. Title of invited talk given by Dr. Patel, "Materials for Science, Communications, and Computers."
- February 8, 1991 — Drs. Bob Spry and S.J. Bai of Wright-Patterson Air Force Base visited Dr. Epstein's office, discussing collaborative research on ladder polymers.
- February 11, 1991 — Dr. Vic Emery of Brookhaven visited Dr. Epstein's laboratory, discussing current research in novel materials, including high temperature superconductors. Title of invited seminar given by Dr. Emery, "Phase Separation and High Temperature Superconductivity."
- February 18, 1991 — Dr. Epstein visited the Department of Physics, Princeton University, Princeton, New Jersey. Title of invited colloquium given by Dr. Epstein, "Three-Dimensionality of Metallic States in Conducting Polymers: Polyaniline."
- February 25 - March 1, 1991 — Professor Andrei Gogolin of the Landau Institute of Theoretical Physics in Moscow, USSR, visited Dr. Epstein's laboratory, discussing current topics in novel conductors. Title of invited seminar given by Professor Gogolin, "Electron Localization in Quasi-1D Organic Conductors."
- March 1-2, 1991 — Professor Jim Tour and Graduate Student Eric Stephens of University of South Carolina visited Dr. MacDiarmid's laboratory. Title of the invited talk given by Dr. Tour, "Synthesis of Conjugated Oligomers and Polymers for Electronic and Photonic Applications."
- March 7-8, 1991 — Dr. MacDiarmid visited Florida State University, Tallahassee. Title of the invited talks given by Dr. MacDiarmid, "Polyaniline: A Novel Type of Conducting Polymer," and "Synthetic Metals: A Novel Role for Organic Polymers."
- March 12, 1991 — Professor Charles Schlichter of the University of Illinois visited Dr. Epstein's office, and presented a colloquium in the Department of Physics.
- March 13, 1991 — Dr. Maxime Nechtschein from Grenoble, France, visited Dr. MacDiarmid's laboratory. Title of the invited talk given by Dr. Nechtschein, "Slow Relaxation and Hysteresis Effects on the Doping of Conducting Polymers."
- March 15, 1991 — Dr. Maxime Nechtschein of the Centre d'Etudes Nuclwaires de Grenoble, France, visited Dr. Epstein's office, discussing research in conducting polymers.
- March 18-22, 1991 — Dr. MacDiarmid and Graduate Students Ms. Yan Sun, Mr. Xun Tang and Mr. Gabriel Asturias attended APS meeting at Cincinnati, Ohio. The following contributed talks were given at Materials Physics topical group special session on conducting polymers (co-organized by Dr MacDiarmid, with Dr. Ray Baughman).

"The Polyanilines: Donnan Equilibrium and Its Effects," G.E. Asturias, G.W. Jang, E.M. Scherr, A.G. MacDiarmid, C. Zhong, K. Doblhofer and H. Reiss.

"Polyaniline Gels: A New Form of Polyaniline," X. Tang, A.G. MacDiarmid and A.J. Epstein.

"Polyaniline: N-Type Doping of Pernigraniline Base," Y. Sun, A.G. MacDiarmid and A.J. Epstein.

"Crystallinity and Texture of Emeraldine Base Films and Fibers," J.E. Fischer, V.B. Cajipe, Q. Zhu, X. Tang, E.M. Scherr, A.R. McGhie and A.G. MacDiarmid.

March 18-22, 1991 — Dr. Epstein, Kim Coplan, Keith Cromack, Gang Du, Mikolaj Jozefowicz, Jingmin Leng, Kwangjoon Kim, Zhaohui Wang, Jiang Yur, Shulai Zhao and Dr. Richard McCall attended APS meeting at Cincinnati, Ohio. The following contributed talks were given at Materials Physics topical group special session on conducting polymers (co-organized by Dr MacDiarmid, with Dr. Ray Baughman).

"Dimensionality of Metallic States and Its Importance for Electron Localization," Z.H. Hwang. (Invited)

"Picosecond Photoinduced Absorption Studies of the 3.0 eV Band of the Emeraldine Base Form of Polyaniline," L.B. Lin, K. Iwata, J.M. Ginder, R.P. McCall, T.L. Gustafson, A.J. Epstein and A.G. MacDiarmid.

"Photoluminescence of Polyaniline and its Derivatives," J.G. Masters, A.G. MacDiarmid, K. Kim, J.M. Ginder and A.J. Epstein.

"Long-Time Behaviour of the Photoinduced FTIR Signal in Polyanilines," M.E. Józefowicz, R.P. McCall, A.J. Epstein, X. Tang, Y. Sun, J.G. Masters and A.G. MacDiarmid.

"Implications of Defective Mass for Erasable Optical Information Storage in Polyaniline," K.A. Coplin, R.P. McCall, J.M. Ginder, A.J. Epstein and A.G. MacDiarmid.

"Anisotropic AC Transport of Oriented, Undoped Polymers," G. Du, A. Burns, Z.H. Wang, A.J. Epstein, D.B. Swanson, N. Theophilou, E.M. Scherr, A.G. MacDiarmid, F. Arnold, C.Y.C. Lee, R. Spray and C.S. Wang.

"Spin Coupling of Photo-Induced Defects in Polyanilines," K.R. Cromack, A.J. Epstein, J.G. Masters, Y. Sun and A.G. MacDiarmid.

"EPR Studies of Pristine N-(CH)_x," Z.H. Wang, A.J. Epstein, D.B. Swanson and A.G. MacDiarmid.

"Charge Localization in Ring-Sulfonated Polyaniline," J. Yue, Z.H. Wang, K.R. Cromack, A.J. Epstein and A.G. MacDiarmid.

"Pernigraniline Base: Peirels vs P-P* Gap," J.M. Leng, R.P. McCall, J.M. Ginder, A.J. Epstein, Y. Sun, S.K. Manohar and A.G. MacDiarmid

"Transport Studies of Fibers of Poly(*o*-ethoxyaniline)," S.L. Zhao, Z.H. Wang A.J. Epstein, S.K. Manohar and A.G. MacDiarmid.

- March 25, 1991 — Dr. Taisuke Yoshioka, from INOAC Corporation, Japan, visited Dr. MacDiarmid's laboratory to discuss research on conducting polymers.
- March 25-26, 1991 — Dr. Epstein visited DuPont in Wilmington, Delaware, to discuss applications of conducting polymers.
- March 27, 1991 — Dr. MacDiarmid spoke at University of Pennsylvania Beckman Center for History of Science in Philadelphia, PA. Title of the invited lecture given by Dr. MacDiarmid, "Synthetic Metals: Past, Present and Future."
- April 5, 1991 — Professor Ronald Hoffmann of Cornell University, Ithaca, New York, visited Dr. Epstein's laboratory, discussing research on electronic structure of novel materials. Title of invited seminar given by Professor Hoffmann, "Making and Breaking Bonds in the Solid State."
- April 5, 1991 — Dr. S. Schmitt-Rink of AT&T Bell Labs visited Dr. Epstein's laboratory, discussing defect states in new materials. Title of invited seminar given by Dr. Schmitt-Rink, "Magnetic Polarons and Excitons in Two Dimensions."
- April 9, 1991 — Representatives from Apple Computers visited Dr. Epstein's office, discussing potential applications of conducting polymers.
- April 10, 1991 — Professor Richard B. Kaner of UCLA, CA visited Dr. MacDiarmid's laboratory. Title of invited talks given by Dr. Kaner, "Rapid Solid State Synthesis of Refractory Materials" and "A New Application for Conducting Polymers."
- April 11, 1991 — Dr. Shobo Bhattacharya of NEC Research Institute in Princeton, New Jersey, visited Dr. Epstein's laboratory, discussing current research in novel conductors. Title of invited seminar given by Dr. Bhattacharya, "Nonlinear Dynamics of Charge Density Wave Conductors."
- April 11-12, 1991 — Drs. Epstein and MacDiarmid visited Dupont Experimental Station, Wilmington, DE and presented a combined talk on "Polyaniline: A Novel Conducting Polymer."
- April 15-19, 1991 — Dr. MacDiarmid attended 201 National ACS Meeting at Atlanta, GA. Title of invited talk given by Dr. MacDiarmid, "Polyaniline: Inter-Relationship Between Ultra-Structure and Properties." In addition, Dr. MacDiarmid participated in a workshop entitled, "Polyaniline Gels: Preparation and Properties."
- April 16-18, 1991 — Dr. Epstein and Jiang Yue attended 201 National ACS Meeting at Atlanta, GA. Title of invited talk given by Dr. Epstein, "Relationship Between Conductivity and Structure and Order in Polyaniline." Title of invited talk given by Jiang Yue, "XPS Study of Sulfonated Polyaniline."
- April 19, 1991 — Dr. Epstein attended the ACS Workshop on the Materials Science of Conductive Polymers in Atlanta, Georgia. Title of invited talk given by Dr. Epstein, "Critical Role of Three-Dimensional Order in Conductive Polymers."
- April 19, 1991 — Kim Coplin, Mikolaj Jozefowicz, Liang Bih Lin and Dr. Richard McCall attended the Poster Session of the Society for Applied Spectroscopy in Columbus, Ohio. Posters presented included:

"Long-Time Behavior of the Photoinduced FTIR Signal in Polyanilines," M.E. Jozefowicz, R.P. McCall, A.J. Epstein, X. Tang, Y. Sun, J.M. Masters and A.G. MacDiarmid.

"Implications of Defect Mass for Erasable Optical Information Storage in Polyaniline," K.A. Coplin, R.P. McCall, J.M. Ginder, A.J. Epstein and A.G. MacDiarmid.

"Picosecond Photoinduced Absorption Studies of the 3.0-eV Band of the Emeraldine Base Form of Polyaniline," L.B. Lin, K. Iwata, T.L. Gustafson, J.M. Ginder, R.P. McCall, A.J. Epstein and A.G. MacDiarmid.

April 22, 1991 — Professor Jean-Luc Bredas, Université de Mons, Belgium, visited Dr. MacDiarmid's laboratory. Title of invited talk given by Dr. Bredas, "The Interconnections Between Chemical, Geometrical and Electronic Structures in Polyanilines."

April 23-24, 1991 — Dr. Jean-Luc Bredas of the Université de Mons, Belgium, visited Dr. Epstein's laboratory, discussing current research in polyanilines and other conducting polymers. Title of invited seminar given by Dr. Bredas, "Novel Concepts in the Theory of Conjugated Molecules: The Aniline Family of Polymers and Nonlinear Optical Response."

April 26, 1991 — Dr. Epstein attended the Centennial Annual Meeting of the Ohio Academy of Sciences. Title of invited talk given by Dr. Epstein, "Conducting Polymers: A New Frontier."

April 28-30, 1991 — Dr. MacDiarmid attended MRS Meeting at Anaheim, CA. Title of invited talk given by Dr. MacDiarmid, "Polyaniline: Conducting Polymers for Technology."

May 1, 1991 — Dr. MacDiarmid met with Professors A.J. Heeger and Paul Smith at the Institute of Polymers and Organic Solids and at Uniax Corporation, Santa Barbara, CA. Title of invited talk given by Dr. MacDiarmid, "Polyaniline: A Novel Class of Conducting Polymers."

May 5-7, 1991 — Drs. MacDiarmid and Epstein attended the 49th ANTEC Meeting in Montreal, Canada. Title of invited talk given by Dr. MacDiarmid, "Polyaniline: Chemical and Physical Basis for Its Processability." Title of invited talk given by Dr. Epstein, "The Chemical Control of Processability, Electromagnetic Response, and Other Properties of Polyanilines and Their Applications to Technologies."

May 7, 1991 — Dr. Yen Wei, along with K. Balasanmugam, M. Olsen, K.G. Owens, K.F. Hsueh and P. Hoontrakul, attended the Sigma Xi Scientific Research Conference, Philadelphia, PA. Title of invited talk given by Dr. Wei, "FAB-Mass Spectroscopic Studies of Polyaniline."

May 20, 1991 — Dr. Yen Wei, along with K. Balasanmugam, M. Olsen, K.G. Owens, K.F. Hsueh and P. Hoontrakul, attended the Mass Spectroscopy Symposium. Title of invited talk given by Dr. Wei, "Mass Spectrometric Characterization of Conductive Polymers."

May 29-31, 1991 — Professor Serge Lefrant and graduate students Guy Louran and Sophie Quillard of the Université de Nantes, France, visited Dr. MacDiarmid's laboratory for discussions on collaborative research. Title of invited talk given by Professor Lefrant, "Resonance Raman Scattering and Photoinduced Absorption in Conjugated Polymers."

May 30, 1991 — Dr. Yen Wei attended The ACS Rockland Section, New York. Title of invited talk given by Dr. Wei, "Plastics That Conduct Electricity."

- June 7-9, 1991 — Dr. MacDiarmid visited Chalmers University at Göteborg, Sweden. Title of invited talk given by Dr. MacDiarmid, "The Polyanilines: A Novel Class of Conducting Polymers."
- June 10-11, 1991 — Dr. Epstein visited Professor Jean-Paul Pouget at the Universite Paris-Sud, Orsay, France, to discuss collaborative research on conducting polymers.
- June 10-12, 1991 — Dr. MacDiarmid visited Linköping University in Linköping, Sweden. Title of invited talk given by Dr. MacDiarmid, "The Polyanilines: A Novel Class of Conducting Polymers."
- June 12, 1991 — Dr. Samuel Shkolnik of the Isreal Atomic Energy Commission in Yavne, Israel, visited Dr. Epstein's laboratory, discussing current research on novel materials.
- June 12-18, 1991 — Dr. Epstein attended Nobel Symposium in Lulea, Sweden on "Conjugated Polymers and Related Materials: The Interconnection of Chemical and Electronic Structures." Title of invited talk by Dr. Epstein, "The Peierls Ground State, Solitons and Polarons in Ring-Containing Polymers."
- June 13-18, 1991 — Dr. MacDiarmid attended Nobel Symposium in Lulea, Sweden on "Conjugated Polymers and Related Materials: The Interconnection of Chemical and Electronic Structures." Title of the plenary lecture given by Dr. MacDiarmid, "The Polyanilines: A Novel Class of Conducting Polymers." Dr. MacDiarmid also chaired a session on "Related Materials" at this symposium.
- June, 1991 — Dr. Farrington and students Michael S. Mendolia, Rokeya Huq, Rene Koksang, P.E. Ponder and B.V.R. Chowdari attended the International Symposium on Polymer Electrolytes III in Annecy, France. Title of contributed talks given by Dr. Farrington and his students are, "Solvation of Cobalt Salts by Oligomeric Polyethers," "Effect of Plasticizers on the Properties of New Ambient Temperature Polymer Electrolytes," and "Studies of Mixed-Cation Effect on a Plasticized-Polymer Electrolyte."
- July 2, 1991 — Mr. Plocher, from NCR in Cambridge, Ohio, visited Dr. Epstein's office, discussing applications of conducting polymers in data aquisition technologies.
- July 15, 1991 — Dr. Hiroshi Koezuka, from Mitsubishi Electric Corporation, Japan, visited Dr. MacDiarmid's laboratory. Title of the invited talk given by Dr. Koezuka, "Field-Effect Transistors Using Conducting Polymers."
- July 18, 1991 — Dr. Nick Castellucci, from Northrup Corporation (Aircraft Division), CA, visited Dr. MacDiarmid's Office. Title of invited talk given by Dr. Castellucci, "Charge Transfer Polymers and Corrosion Inhibition."
- July 18, 1991 — Drs. Epstein, Andrew Burns and Richard McCall visited Dr. Robert Spry and others at Wright-Patterson Air Force Base, Dayton, Ohio, discussing collaborative research on ladder polymers.
- July 26, 1991 — Dr. Epstein visited Dr. Steven Feinberg and Dr. S.A. Goldstein at the University of Michigan, discussing potential biological applications of conducting polymers.
- July 30, 1991.— Dr. Wei visited Imperial Chemical Industries, PA. Title of invited talk given by Dr. Wei, "Development of a New Technology for Synthesis of Conductive Polymers."
- August 8, 1991 — Dr. Epstein visited Dupont, Wilmington, Delaware, discussing applications of conducting polymers.

August 9, 1991 — Dr. Nobuo Sasaki, from Fujitsu Ltd., Japan, visited Dr. MacDiarmid's office. Title of invited talk given by Dr. Sasaki, "Selective Fabrication of Polyacetylene wire and Electrical Characteristics of Polyacetylene FETS."

August 12, 1991 — Dr. Sasaki of Fujitsu Limited, Kawasaki, Japan, visited Dr. Epstein's office, discussing research in conducting polymers.

August 14, 1991 — Dr. Andrew Monkman, from Applied Physics Dept., University of Durham, UK, visited Dr. MacDiarmid's laboratory. Title of informal seminar given by Dr. Monkman, "Polyaniline: A Question and (Hopefully) Answer Session."

August 19-23, 1991 — Dr. Epstein attended the International Conference on Optical Probes of Conjugated Polymers at Snowbird, Utah. Two presentations were given:

"Long-Lived Photoinduced Phenomena in Polyaniline and Applications to Optical Information Storage," A.J. Epstein, R.P. McCall, M.E. Jozefowicz, K.R. Cromack, K.A. Coplin and A.G. MacDiarmid. (Invited)

"Picosecond Photoinduced Absorption Studies of Polyaniline," L.B. Lin, K. Kim, K. Iwata, J.M. Ginder, R.P. McCall, T.L. Gustafson, A.J. Epstein and A.G. MacDiarmid.

August 25-30, 1991 — MacDiarmid presented an invited lecture at ACS National Meeting, New York, in a special session on Conjugated Polymers in the Division of Polymer Chemistry program. Title of invited lecture given by Dr. MacDiarmid, "The Polyanilines: A Novel Class of Conducting Polymers."

September 3, 1991 — Professor Wu-Pei Su, University of Houston, began a 6-month appointment as a Visiting Professor at Ohio State University.

September 5, 1991 — Dr. David Burley, Techline Corporation, Parsippany, New Jersey, visited Dr. Epstein's office, discussing applications of conducting polymers.

September 12, 1991 — Professor Keu-Hong Kim, from Yonsei University, Korea, visited Dr. MacDiarmid's office for discussion on conducting polymers.

September 20, 1991 — Dr. Epstein attended a review committee meeting on the electroactive polymers program at Brookhaven National Laboratory.

September 20, 1991 — Dr. Wei visited Southern Illinois University, Carbondale, Illinois. Title of invited talk given by Dr. Wei, "Electrically Conductive Polymers and Their Applications."

September 26, 1991 — Mr. Robert Baird of NCR in Cambridge, Ohio visited Dr. Epstein's to discuss applications of conducting polymers.

APPENDIX

D

PUBLICATIONS & PATENTS

Publications

1. Papers Published

(Acknowledging URI and Other Support)

(i) Epstein and/or MacDiarmid (OSU and/or Penn)

"Polyanilines: A Novel Class of Conducting Polymers," Faraday Discuss. Chem. Soc., **88**, 317 (1989), A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI)

"Highly Conducting Polyanilines and Polyacetylene/Polyaniline Composites," in Electronic Properties of Conjugated Polymers, H. Kuzmany, M. Mehring and S. Roth, Eds., **91**, 29 (1989), N. Theophilou, A.G. MacDiarmid, D. Djurado, J.E. Fischer and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-86-15475, NSF-MRL Grant No. 85-19059 and in part by DOE Grant No. DE-FGO2-87-ER 45254)

"Influence of Catalyst on the Structure and Conductivity of Highly Conducting Polyacetylenes," in Electronic Properties of Conjugated Polymers, H. Kuzmany, M. Mehring and S. Roth, Eds., **91**, 14 (1989), N. Theophilou, D.B. Swanson, A.G. MacDiarmid, J.G. Mantovani, B.K. Annis and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-86-15475 and in part by DOE Contract No. DE-ACU5-84-OR 21400)

"Polyaniline: Synthesis and Characterization of Pernigraniline Base," J. Chem. Soc. Chem. Commun., 529 (1990), Y. Sun, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by University of Pennsylvania)

"Aniline Tetramers: Comparison with Aniline Octamer and Polyaniline," J. Phys. & Chem. Solids, **51**, 107 (1990), H.H.S. Javadi, S.P. Treat, J.M. Ginder, J.E. Wolf and A.J. Epstein. (Supported in part by URI and in part by Allied Signal Corporation)

"Ring-Rotational Dimerization in Pernigraniline," Phys. Rev. Lett., **64**, 1184 (1990), J.M. Ginder and A.J. Epstein. (Supported in part by URI)

"The Role of Ring Torsion Angle in Polyaniline: Electronic Structure and Defect States," Phys. Rev. B, **41**, 10674 (1990), J.M. Ginder and A.J. Epstein. (Supported in part by URI)

"Synthesis of Self-Doped Conducting Polyaniline," J. Am. Chem. Soc., **112**, 2800 (1990), J. Yue and A.J. Epstein. (Supported in part by URI)

"New Developments in the Synthesis and Doping of Polyacetylene and Polyaniline," in Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics and Molecular Electronics, J.L. Bredas and R.R. Chance, Eds., Kluwer Academic Publishers, Dordrecht, p. 53 (1990), A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI)

"Polyaniline versus Polyacetylene, or Rings versus Bonds and The Role of Barriers and Crystallinity," in Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics and Molecular Electronics, J.L. Bredas and R.R. Chance, Eds., Kluwer Academic Publishers, Dordrecht, p. 195 (1990), A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI)

"Investigation of Surface Morphology of Emeraldine Hydrochloride by Scanning Tunneling Microscopy," J. Appl. Polym. Sc., **40**, 1693 (1990), J.G. Mantovani, R.J. Warmack, B.K. Annis, A.G. MacDiarmid and E. Scherr. (Supported in part by URI and in part by ORNL Laboratory Director's R & D Fund and in part by DOE Contract No. DE-ACO5-84OR21400 with the Martin Marietta Energy Systems, Inc.)

"Phenyl Ring Rotations, Structural Order and Electronic States in Polyaniline," Synth. Met., **37**, 45 (1990), J.M. Ginder, A.J. Epstein and A.G. MacDiarmid. (Supported in part by URI)

"Sulfonic Acid Ring-Substituted Polyaniline, A Self-Doped Conducting Polymer," Mol. Cryst. Liq. Cryst., **189**, 255 (1990), J. Yue, A.J. Epstein and A.G. MacDiarmid. (Supported in part by URI)

"Non-Ohmic Conductivity: A Probe of the Localization Mechanism in Polyaniline Derivatives," Mol. Cryst. Liq. Cryst., **189**, 263 (1990), Z.H. Wang, E. Ehrenfreund, A. Ray, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059)

"Electron Localization in Polyaniline Derivatives," Phys. Rev. B. Rapid Commun., **42**, 5411 (1990), Z.H. Wang, H.H.S. Javadi, A. Ray, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059)

"Rupture of Cobalt-Iron and Oxygen Bonds in the Chain During Thermal Treatment of $\text{YBa}_2\text{Cu}_3(^{57}\text{Co})\text{O}_{6.0}$: Emission Mössbauer Studies," Physica C, **171**, 406-414 (1990). (Supported in part by URI.)

"The Polyanilines: Potential Technology Based on New Chemistry and New Properties," in Science and Applications of Conducting Polymers, W.R. Salaneck, D.T. Clark and E.J. Samuelsen, Eds., IOP Publishing Ltd., Bristol, U.K., p. 117 (1990), A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-88-19885)

"The Controlled Electromagnetic Response of Polyanilines and Its Application To Technologies," in Science and Applications of Conducting Polymers, W.R. Salaneck, D.T. Clark and E.J. Samuelsen, Eds., IOP Publishing Ltd., Bristol, U.K., p. 141 (1990), A.J. Epstein and A.G. MacDiarmid. (Supported in part by URI)

"Comment on 'Role of Disorder in the Conduction Mechanism of Polyanilines,'" Phys. Rev. B, **65**, 526 (1990), J.-L. Bredas, A.J. Epstein and A.G. MacDiarmid.

"Spin Dynamics and Conductivity in Polyaniline," Phys. Rev. B, **65**, 664 (1990), A.J. Epstein, A.G. MacDiarmid and J.-P. Pouget.

"Highly Conducting Polyacetylene: Three-Dimensional Delocalization," Phys. Rev. B, **43**, 2183 (1991), H.H.S. Javadi, A. Chakraborty, C. Li, N. Theophilou, D.B. Swanson, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI)

"Torsional Defects and Photoinduced Charge Transfer In Ring Containing Polymers," Mol. Cryst. Liq. Cryst., **194**, 13 (1991), J.M. Ginder, A.J. Epstein and A.G. MacDiarmid. (Supported in part by URI)

"X-Ray Structure of Polyaniline," Macromolecules, **24**, 779 (1991), J.P. Pouget, M.E. Józefowicz, A.J. Epstein, X. Tang and A.G. MacDiarmid. (Supported in part by URI and in part by NSF International Grant No. INT-85-14202 and in part by Action Initiative CNRS-NSF)

"Electron Localization and Charge Transport in Poly(o-toluidine): A Model Polyaniline Derivative," Phys. Rev. B, **43**, 4373 (1991), Z.H. Wang, A. Ray, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF-MRL Grant No. DMR-85-19059)

"Three Dimensionality of 'Metallic' States in Conducting Polymers: Polyaniline," Phys. Rev. Lett., **66**, 1745 (1991), Z.H. Wang, C. Li, E.M. Scherr, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI.)

"Effect of Sulfonic Acid Group on Polyaniline Backbone," J. Am. Chem. Soc., **113**, 2665 (1991), J. Yue, Z.H. Wang, K.R. Cromack, A.J. Epstein and A.G. MacDiarmid. (Supported in part by URI.)

"Polarized Absorption In Oriented 'New' (CH)_x, Proceed, I.C.S.M., Tubingen, Synth. Met., **41**, 159 (1991), H.S. Woo, D.B. Tanner, N. Theophilou, and A.G. MacDiarmid. (Supported in part by URI.)

"Structure, Order, and the Metallic State in Polyaniline and its Derivatives," Proceed, I.C.S.M. Tubingen, Synth. Met., **41**, 601 (1991), A.J. Epstein and A.G. MacDiarmid. (Supported in part by URI.)

"Polyaniline: Synthesis and Properties of Pernigraniline Base," Proceed, I.C.S.M. Tubingen, Synth. Met., **41**, 621 (1991), A.G. MacDiarmid, S.K. Manohar, J.G. Masters, Y. Sun, H. Weiss and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-88-19885.)

"Light Induced Electron Spin Resonance in Polyaniline," Proceed, I.C.S.M. Tubingen, Synth. Met., **41**, 641 (1991), K. Cromack, A.J. Epstein, J.G. Masters, Y. Sun and A.G. MacDiarmid. (Supported in part by URI.)

"Polyaniline: Pernigraniline, An Isolable Intermediate in the Conventional Chemical Synthesis of Emeraldine," Proceed, I.C.S.M. Tubingen, Synth. Met., **41**, 711 (1991), S.K. Manohar, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-88-19885.)

"Polyaniline: Allowed Oxidation States," Proceed, I.C.S.M. Tubingen, Synth. Met., **41**, 715 (1991), J.G. Masters, Y. Sun, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI.)

"X-Ray Structure of Polyaniline," Proceed, I.C.S.M. Tubingen, Synth. Met., **41**, 723 (1991), M.E. Jozefowicz, A.J. Epstein, J.P. Pouget, J.G. Masters, A. Ray, Y. Sun, X. Tang and A.G. MacDiarmid. (Supported in part by URI and in part by NSF Int. Grant No. INT-8514202 and in part by "Action-Initiative CNRS-NSF.")

"Polyaniline: Oriented Films and Fibers," Proceed, I.C.S.M. Tubingen, Synth. Met., **41**, 735 (1991), E.M. Scherr, A.G. MacDiarmid, S.K. Manohar, J.G. Masters, Y. Sun, X. Tang, M.A. Druy, P.J. Glatkowski, V.B. Cajipe, J.E. Fischer, K.R. Cromack, M.E. Jozefowicz, J.M. Ginder, R.P. McCall and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-88-19885.)

"Electron Localization in Polyaniline and Its Derivatives," Proceed, I.C.S.M. Tubingen, Synth. Met., **41**, 749 (1991), Z.H. Wang, A.J. Epstein, A. Ray and A.G. MacDiarmid. (Supported in part by URI.)

"Thermal Stabilities of Polyanilines," Proceed, I.C.S.M. Tubingen, Synth. Met., 41, 765 (1991), J. Yue, A.J. Epstein, Z. Zhong, P.K. Gallagher and A.G. MacDiarmid. (Supported in part by URI.)

"Photoexcitation Spectroscopy of Pernigraniline," Proceed, I.C.S.M. Tubingen, Synth. Met., 41, 1311 (1991), J.M. Leng, J.M. Ginder, R.P. McCall, H.J. Ye, A.J. Epstein, Y. Sun, S.K. Manohar and A.G. MacDiarmid. (Supported in part by URI.)

"Photoinduced Absorption and Erasable Optical Information Storage in Polyanilines," Proceed, I.C.S.M. Tubingen, Synth. Met., 41, 1329 (1991), R.P. McCall, J.M. Ginder, J.M. Leng, K.A. Coplin, H.J. Ye, A.J. Epstein, G.E. Asturias, S.K. Manohar, J.G. Masters, E.M. Scherr, Y. Sun and A.G. MacDiarmid. (Supported in part by URI.)

"Impedance Profiling: A Convenient Technique for Determining the Redox or Protonic Acid Doping Characteristics of Conducting Polymers," Proceed, I.C.S.M. Tubingen, Synth. Met., 43, 2987 (1991), D.B. Swanson, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-88-19885.)

"Ring-Torsional Polarons in Polyaniline and Polyparaphenylene Sulfide," Proceed, I.C.S.M. Tubingen, Synth. Met., 43, 3431 (1991), J.M. Ginder, A.J. Epstein and A.G. MacDiarmid. (Supported in part by URI.)

"The Chemical Control of Processibility, Electromagnetic Response and Other Properties of Polyanilines and Their Applications to Technologies," ANTEC '91, p. 755, (Proceed. Society of Plastics Engineers Annual Technical Conference, Montreal, Canada, May 5-9, 1991), A.J. Epstein and A.G. MacDiarmid. (Supported in part by URI.)

"Polyaniline/PPD-T Fibers," Synth. Met., 41, 1005 (1991), C.H. Hsu, P. Vaca-Segonds and A.J. Epstein.

"Spectroscopy and Photoexcitation Spectroscopy of Polyaniline: A Model System for New Phenomena," in Spectroscopy of advanced Materials, Clark and Hester, eds., (1991), A.J. Epstein, R.P. McCall, J.M. Ginder and A.G. MacDiarmid.

"The Polyanilines: Model System for Diverse Electronic Phenomena," in Conjugated Polymers, Bredas and Silbey, eds., pp. 211-224 (1991), A.J. Epstein.

"XPS Study of Self-Doped Conducting Polyaniline and Parent Systems," Macromolecules, 24, 4441 (1991), J. Yue and A.J. Epstein.

"Ring-Torsional Solitons in Polyaniline," Phys. Rev. B, 44, 2362 (1991), R. MacKenzie, J.M. Ginder and A.J. Epstein.

"Influence of Ring-Torsional Dimerization on the Band Gap of Aromatic Conjugated Polymers," Phys. Rev. B, 44, 6002 (1991), J.L. Bredas, C. Quattrocchi, A.G. MacDiarmid, J.M. Ginder and A.J. Epstein.

"Thermal Process for Orientation of Polyaniline Films," Macromolecules, 24, 4157 (1991), K.R. Cromack, M.E. Jozefowicz, J.M. Ginder, A.J. Epstein, R.P. McCall, G. Du, J.M. Leng, K. Kim, C. Li, Z.H. Wang, M.A. Drury, P.J. Glatkowski, E.M. Scherr and A.G. MacDiarmid. (Supported in part by URI and in part by U.S. Air Force Office of Scientific Research.)

"The Polyanilines: A Novel Class of Conducting Polymers," Polymer Preprints, 32-3, 709 (1991), A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-88-19885.)

"The Polyaniline: Recent Advances in Chemistry and Processing" in Lower-Dimensional Systems and Molecular Electronics, R.M. Metzger, et al. Eds., Plenum Press, New York, p. 303 (1991), A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI.)

"Polyaniline: New Physics In An Old Polymer," in Lower-Dimensional Systems and Molecular Electronics, R.M. Metzger, et al. Eds., Plenum Press, New York, p. 335 (1991), A.J. Epstein and A.G. MacDiarmid. (Supported in part by URI.)

(ii) Farrington (Penn)

"Crystallinity and Thermomechanical Properties of Lead Halide-PEO Complexes," Solid State Ionics, 40/41, B3 (1990), A. Wensjö, J.O. Thomas, G.K. Jones and G.C. Farrington. (Supported in part by URI)

"Conductivity in PEO-Based Zn(II) Polymer Electrolytes," Solid State Ionics, 40/41, 663 (1990), H. Yong, R. Huq and G.C. Farrington. (Supported in part by URI)

"Thermogravimetry - Mass Spectrometry Using a Simple Capillary Interface," American Laboratory, 22(1), 21 (1990), E.L. Charsley, S.B. Worrington, G.K. Jones and A.R. McGhie. (Supported in part by URI)

(iii) Wei/MacDiarmid/Epstein (Drexel/Penn/OSU)

"Spectroscopic and Molecular Weight Studies of Polytoluidines", Mater. Res. Soc. Symp. Proc., Vol. 173, pp. 341-346 (1990), Y. Wei, K.F. Hsueh, S. Nagy, A. Ray, A.G. MacDiarmid, J. Dykins, A.J. Epstein, and G.E. Wnek. (Supported in part by URI and in part by ACS-PRF)

(iv) Wei (Drexel U.)

"Polymerization of Aniline and Alkyl Ring-Substituted Anilines in the Presence of Aromatic Additives", J. Phys. Chem., Vol. 94, pp. 7716-7721 (1990), Y. Wei, G.-W. Jang, K.F. Hsueh, C.-C. Chan, R. Hariharan, S.A. Patel, and C.K. Whitecar. (Supported in part by URI and in part by ACS-PRF and in part by Drexel University)

"Synthesis, Polymerization and Thermal Properties of A New Acetylene-Terminated Aromatic Schiff Base," J. Polym. Sci. A: Polym. Chem., 29, 749-758 (1991), Y. Wei, R. Hariharan and J.K. Ray. (Supported in part by URI and in part by Drexel Research Scholar Award to Dr. Yen Wei.)

"Electrochemical Polymerization of Thiophenes in the Presence of Bithiophene or Terthiophene, Kinetic and Mechanism of the Polymerization," Chem. Mater., 3, 888 (1991), Y. Wei, C.-C. Chan, G.-W. Jang and J. Tian. (Supported in part by URI)

"Mass Spectrometric Characterization of Conductive Polymers," Proceed., ASMS Conference on MS and Allied Topics, 39, 408 (1991), K. Balasubramanian, M. Olsen, K.G. Owens, Y. Wei, K.F. Hsueh and P. Hoontrakul. (Supported in part by URI)

(v) Yang (U. Rhode Island)

"The 0.9 eV Absorption Band of Polyaniline: A Morphologically Sensitive Electronic Absorption," Mat. Res. Soc. Sym. Proc., 173, 305 (1990), D. Zhang, J.-H. Hwang and S.C. Yang. (Supported in part by URI and in part by NSF under Grant #CHE-8216482.)

"Polyaniline as a Reversibly Switchable Electrochromic Material," Mat. Res. Soc. Sym. Proc., 173, 329 (1990), W.-R. Shieh, S.C. Yang, C. Marzzacco and J.-H. Hwang. (Supported in part by URI and in part by PPG Industries.)

Publications

2. Papers Accepted/Submitted for Publication

(Acknowledging URI and Other Support)

(i) Epstein and/or MacDiarmid (OSU and/or Penn)

"Erasable Optical Information Storage in Polyaniline," Appl. Phys. Lett., submitted (1990), R.P. McCall, J.M. Ginder and A.J. Epstein. (Supported in part by URI)

"Polyaniline: Inter-relationship Between Ultra-Structure and Properties," PMSE Preprints, (Accepted 1990), A.G. MacDiarmid, S.K. Manohar, E.M. Scherr, X. Tang, M.A. Druy, P.J. Glatkowski and A.J. Epstein. (Supported in part by URI)

"Synthetic Metals: A Novel Role for Organic Polymers," Proceed., International Symposium on Speciality Polymers, Singapore, Die Makromolekulare Chemie, In Press (1991), A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-88-19885)

"Novel Concepts in Electronic Polymers: Polyaniline and Its Derivatives," Proceed., International Symposium on Speciality Polymers, Singapore, Die Makromolekulare Chemie, In Press (1991), A.J. Epstein and A.G. MacDiarmid. (Supported in part by URI)

"Spectroscopy and Photoexcitation Spectroscopies of Polyaniline: A Model System for New Phenomena," in Spectroscopy of Advanced Materials, R.J.H. Clark and R.E. Hester, Eds., John Wiley, New York (In Press 1991), A.J. Epstein, R.P. McCall, J.M. Ginder and A.G. MacDiarmid. (Supported in part by URI)

"XPS Study of Sulfonated Polyaniline," PMSE Preprints, (In Press 1991), J. Yue, A.J. Epstein and A.G. MacDiarmid. (Supported in part by URI.)

"Photoexcitation in Pernigraniline: Ring-Torsional Polarons and Bond-Order Solitons," Phys. Rev. Lett., (In Press 1991), J.M. Leng, J.M. Ginder, R.P. McCall, H.J. Ye, Y. Sun, S.K. Manohar, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI.)

"X-Ray Structure of Polyaniline Derivative-Poly-Ortho-Toluidine: The Structural Origin of Charge Localization," Macromolecules, (In Press 1991), M.E. Jozefowicz, A.J. Epstein, J.P. Pouget, J.G. Masters, A. Ray and A.G. MacDiarmid. (Supported in part by URI.)

"Science and Technology of Conducting Polymers," in *Frontiers of Polymer Research*, P.N. Prasad and J.K. Nigam, eds., Plenum Press, New York, (In Press 1991), A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-88-19885.)

"Electronic Phenomena in Polyanilines," in *Frontiers of Polymer Research*, P.N. Prasad and J.K. Nigam, eds., Plenum Press, New York, (In Press 1991), A.J. Epstein and A.G. MacDiarmid. (Supported in part by URI and in part by NSF Grant No. DMR-88-19885.)

"EPR of Naarmann-Theophilou Polyacetylene: Critical Role of Interchain Interactions," *Phys. Rev. B*, (Submitted, July 1991), Z.H. Wang, N. Theophilou, D.B. Swanson, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI.)

"Molecular/Organic/Polymeric Ferro-Magnets: Design, Synthesis and Physical Properties," *Synth. Met.*, (In Press 1991), A.J. Epstein and J.S. Miller.

"Application of Microwave Cavity Perturbation Techniques in Conducting Polymers," *IEEE Instrumentation/Measurement Technology Conference*, (In Press 1991), Z.H. Wang, H.H.S. Javadi and A.J. Epstein.

"Intrachain Dynamics and Interchain Structures of Polymers: A Comparison of Polyacetylene, Polyaniline and Poly(Paraphenylene-Vinylene)," *Phys. Rev. B*, (In Press 1991), J. Ma, J.E. Fischer, E.M. Scherr, A.G. MacDiarmid, M.E. Jozefowicz, A.J. Epstein, C. Mathis, B. Francois, N. Coustel and P. Bernier.

"Protonic Acid Doping of Two Classes of the Emeraldine Form of Polyaniline," *Synth. Met.*, (In Press 1991), M.E. Jozefowicz, A.J. Epstein and X. Tang.

"Proton Transport on Modified Sulfonated Polyaniline Backbone," *J. Am. Chem. Soc.*, (In Press 1991), J. Yue and A.J. Epstein.

"Synthesis and Conductivity of Copolymer of 4-4'-Diaminodiphenylamine and Terephthaloyl Chloride," *Polymer*, (In Press 1991), G. Gordon, J. Yue and A.J. Epstein.

"The Peierls Ground State, Solitons and Polarons in Ring-Containing Polymers," in *Conjugated Polymers & Related Materials: The Interconnection of Chemical & Electronic Structure*, (In Press 1991), A.J. Epstein.

(ii) Farrington (Penn)

"Studies of the Stability of Poly(ethylene oxide) and PEO-Based Solid Electrolytes Using Thermogravimetry - Mass Spectrometry," *Macromolecules*, submitted (1990), G.K. Jones, A.R. McGhie and G.C. Farrington. (Supported in part by URI)

"Electrochemical and Chemical Characteristics of New Ambient-Temperature Lithium Polymer-Electrolyte," in *Primary and Secondary Lithium Batteries*, *J. Electrochem. Soc.*, submitted (1990), R. Huq, G.C. Farrington, R. Koksang and P.E. Tonder. (Supported in part by URI)

"Characterization of Polymer Electrolytes by Simultaneous TMA-DETA Techniques," chapter in *Materials Characterization by Thermo-mechanical Analysis*, A. Riga and M. Neag, Eds., submitted (1990), A.R. McGhie, G.F. Jones, G.C. Farrington and E. Paul. (Supported in part by URI)

"Solvation of Cobalt Salts by Oligomeric Polyethers," *J. Interfac. Electrochem.*, (Submitted 1991), M.S. Mendolia and G.C. Farrington. (Supported in part by URI.)

"Effect of Plasticizers on the Properties of New Ambient Temperature Polymer Electrolytes," J. Interfac. Electrochem., (Submitted 1991), R. Huq, R. Koksang, P.E. Tonder and G.C. Farrington. (Supported in part by URI.)

"Studies of Mixed-Cation Effect on a Plasticized-Polymer Electrolyte," J. Interfac. Electrochem., (Submitted 1991), B.V.R. Chowdari, R. Huq and G.C. Farrington. (Supported in part by URI.)

"Poly(ethylene oxide) Electrolytes Containing Mixed Salts," J. Polym. Sci. B, (Submitted 1991), H. Yang and G.C. Farrington. (Supported in part by URI.)

"Poly(ethylene oxide)-based Zn(II) Halide Electrolytes," J. Electrochem. Soc., (Submitted 1991), H. Yang and G.C. Farrington. (Supported in part by URI.)

"The Effect of Low Molecular Weight Additives on the Properties of Poly(ethylene oxide)-based Zn(II) and Li(I) Electrolytes," Macromolecules, (Submitted 1991), H. Yang, L.L. Yang and G.C. Farrington. (Supported in part by URI.)

"Studies of the Stability of Poly(ethylene oxide) and PEO-Based Solid Electrolytes Using Thermogravimetry-Mass Spectrometry," Macromolecules, (Submitted 1991), G.K. Jones, A.R. McGhie and G.C. Farrington. (Supported in part by URI.)

"The Study of Polyether Solvation Mechanisms Using UV/Vis Spectroscopy," Polym. Electrolyte Rev., (In Press 1991), M. Mendolia, H. Cai and G.C. Farrington. (Supported in part by URI.)

(iii) Wei (Drexel U.)

"Synthesis, Polymerization and Thermal Properties of A New Acetylene-Terminated Aromatic Schiff Base," J. Polym. Sci., Polym. Chem. Ed., In Press (1991), Y. Wei, R. Hariharan and J.K. Ray. (Supported in part by URI and in part by Drexel University)

"A New Method for Polymerization of Pyrrole and Its Derivatives," Makromol. Chem., Rapid Commun., (Submitted 1991), Y. Wei, J. Tian and D.C. Yang. (Support in part by URI and in part by Du Pont Company.)

"Thermal Transitions and Mechanical Properties of Chemically Prepared Polyaniline," Polymer, (In Press 1991), Y. wei, G.-W. Jang, K.F. Hsueh, E.M. Scherr, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by ACS-PRF and in part by Drexel Research Scholar Award to Dr. Yen Wei.)

"A Gel-Permeation Chromatography Study of Electrochemically Synthesized Poly(3-alkylthiophenes)," Polym. Comm., (In Press 1991), Y. Wei and J. Tian.

"FAB Mass Spectroscopy of Chemically Prepared Polyanilines," J. Am. Soc. Mass Spec., (In Press 1991), K. Balasanmugan, K.G. Owens, K.F. Hsueh, P. Hoontrakul, Y. Wei and M. Olsen.

(iv) Wei/MacDiarmid/Epstein (Drexel/Penn/OSU)

"Thermal Transitions and Mechanical Properties of the Films of the Chemically Prepared Polyaniline," Polymer, (In Press 1991), Y. Wei, G.-W. Jang, K.F. Hsueh, E.M. Scherr, A.G. MacDiarmid and A.J. Epstein.

Patents (4/1/90 - 9/30/91)

Patents resulting from URI support

Drexel University (Wei)

"A Novel Synthesis of Polythiophene and Its Derivatives," Y. Wei, G.-W. Jang and C.-C. Chan. U.S. Patent No. 4,986,886 (1991). (Supported in part by URI and in part by Drexel University - Office of Sponsored Research Projects (85%).)

OSU (Epstein)

"Resistive Films," Mammino, A.J. Epstein. U.S. Patent No. 07/458,443 (June 14, 1991).

Penn (MacDiarmid)

U.S. Patent #4,935,181, Issued June 19, 1990, N. Theophilou, S. Manohar, E. Scherr, "Process of Making Oriented Films of Conductive Polymers."

U.S. Patent #5,023,149, Issued June 11, 1991, A. G. MacDiarmid and N. L. D. Somasiri, "Electrochemistry Employing Polyanilines."

Patents Applied

Penn (MacDiarmid)

UP No. 0778, Penn No. E-852, A.G. MacDiarmid and Sanjeev Manohar, "Synthesis of High Molecular Weight Polyaniline." Filed November 7, 1991.

UP No. 0617, Penn No. D-774, A.G. MacDiarmid and X. Tang, "Cross-Linked Polymers Derived from Polyaniline and Gels Comprising the Same." Filed February 13, 1991.

OSU (Epstein)

"Sulfonated Polyaniline Compositions, Ammonium Salts Thereof, Processes for Their Preparation and Uses Thereof," A.J. Epstein and J. Yue. Filed, May 25, 1990.

"Processes for Preparation of Sulfonated Polyaniline Compositions and Uses Thereof," A.J. Epstein and J. Yue. Filed, May 25, 1990.

"Processes for Forming Fibers of Sulfonated Polyaniline Compositions and Uses Thereof," A.J. Epstein and J. Yue. Filed, May 25, 1990.

"Compositions of Insulating Polymers and Sulfonated Polyaniline Compositions and Uses Thereof," A.J. Epstein and J. Yue. Filed, May 25, 1990.

"Sulfonated Polyaniline Salt Compositions and Uses Thereof," A.J. Epstein and J. Yue. Filed, May 25, 1990.

Drexel (Wei)

"A New Synthesis of Electroactive Polypyrrole and Derivatives," Y. Wei, D.C. Yang and J. Tian. (Supported in part by URI and in part by Drexel University - Office of Sponsored Research Projects (50%).)

Patent Disclosures

Penn (MacDiarmid)

A.G. MacDiarmid, "A Thermally Stable Conducting Polymer Salt." Disclosed, October 2, 1990.

A.G. MacDiarmid, "Gels, Elastomers and Blends of Polyaniline and Its Derivatives." Disclosed, December 14, 1990.

A.G. MacDiarmid and G. Asturias, "A Method for Synthesis of High Molecular Weight Polyaniline." Disclosed, April 3, 1991.

A.G. MacDiarmid and Sanjeev Manohar, "Living Polymerization and the Route to Polyaniline." Disclosed, June 21, 1991.

APPENDIX

E

FISCAL BUDGET (BY QUARTER)

4/1/90 — 9/30/91

Page 1

[illegible]

[illegible]

FISCAL STATUS	EXPENDITURES AND COMMITMENTS						
A. University of Pennsylvania: The following represents monies spent and/or committed to that portion of the program carried on at the University of Pennsylvania.							
	1 Budgeted 1st Year	2 Budgeted 2nd Year	3 Budgeted 3rd Year	4 Budgeted 4th Year	5 Budgeted 5th Year	6 Total Spent	7 Available Balance
U of P (Chem)	\$727,044	\$577,611	\$638,019	\$995,650	\$887,206	\$2,656,830	\$1,166,800
(Dr. A. G. MacDiarmid)							
U of P (MSE)	\$231,565	\$309,845	\$180,417	\$249,195	\$522,886	\$1,054,124	\$419,784
(DR. G. C. FAIVINGTON)							
B. SUBCONTRACTS							
OBJ	\$867,116	\$369,597	\$277,808	\$546,955	\$508,707	\$2,234,362	\$335,821
DR. A. J. EPSTEIN							
LOCKEED	\$87,037	\$87,037	\$69,102	\$200,000	\$200,000	\$353,176	\$280,000
MANNING	\$37,143	\$30,246	\$0	0	\$0	\$67,389	\$0
(MS. M. DOLTON)							
Dr. White							
MIT	\$38,896	\$0	\$0	\$0	\$0	\$38,896	\$0
FTI	\$38,006	\$69,940	\$51,628	\$0	\$0	\$157,774	\$0
UNIV. OF CALIF. (SAN DIEGO)	\$31,862	\$31,862	\$25,913	\$36,000	\$36,000	\$150,674	\$10,863
(DR. S. C. YANG)							
MONTGOMERY STATE	\$29,231	\$31,862	\$25,913	\$36,000	\$36,000	\$130,671	\$28,335
(DR. B. D. HUMPHREY)							
KENT STATE	\$0	\$0	\$0	\$350,000	\$350,000	\$313,075	\$386,925
(DR. W. DOANE)							
CASE WESTERN	\$0	\$0	\$0	\$100,000	\$100,000	\$148,472	\$53,528
(DR. V. FENCEC)							
UNC	\$0	\$0	\$0	\$150,000	\$150,000	\$185,460	\$134,540
(DR. E. T. SAMUKSKO)							
Drexel Univ.	\$0	\$0	\$0	\$36,000	\$36,000	\$41,670	\$30,330
(DR. V. WIEN)							
BUDGET BALANCE							
							\$1,016,900
							\$419,784
							\$335,821
							\$280,000
							\$0
							\$0
							\$10,863
							\$28,335
							\$386,925
							\$53,528
							\$134,540
							\$30,330

FISCAL STATUS EXPENDITURES AND COMMITMENTS	The following represents monies spent and/or committed to that portion of the program carried on at the University of Pennsylvania.						
	1 Budgeted 1st Year	2 Budgeted 2nd Year	3 Budgeted 3rd Year	4 Budgeted 4th Year	5 Budgeted 5th Year	6 Total Spent	7 Available Balance
A. University of Pennsylvania: The following represents monies spent and/or committed to that portion of the program carried on at the University of Pennsylvania.							
U of P (Chem)	9/15/86 - 9/30/87 \$727,044	10/1/87 - 9/30/88 \$577,611	10/1/88 - 9/30/89 \$638,019	11/1/89 - 10/30/91 \$995,950	11/1/90 - 12/30/91 \$887,206	9/15/86 - 6/30/91 \$2,928,125	6/30/91 \$897,605
(Dr. A. G. MacDiarmid)							
U of P (MSE)	\$231,565	\$309,845	\$180,417	\$249,195	\$522,866	\$1,144,114	\$329,784
DR G. C. FARRINGTON							
B. SUBCONTRACTS							
OSU	\$967,116	\$369,597	\$277,008	\$546,955	\$508,707	\$2,380,034	\$190,149
DR A. J. EPSTEIN							
LOCKHEED	\$87,037	\$87,037	\$69,102	\$200,000	\$200,000	\$371,176	\$272,000
MM INC.	\$37,143	\$30,248	\$0	0	\$0	\$67,389	\$0
(MS. M. DOLTON)							
Dr. Week							
MIT	\$36,996	\$0	\$0	\$0	\$0	\$36,996	\$0
ITT	\$36,006	\$69,940	\$51,826	\$0	\$0	\$157,774	\$0
UNIV. RHODE ISLAND	\$31,962	\$31,862	\$25,913	\$36,000	\$36,000	\$154,174	\$7,463
(DR. S. C. YANG)							
MONTCLAR STATE	\$29,231	\$31,862	\$25,913	\$36,000	\$36,000	\$137,491	\$21,515
(DR. B. D. HUMPHREY)							
KENT STATE	\$0	\$0	\$0	\$350,000	\$350,000	\$500,575	\$199,425
(DR. W. DOANE)							
CASE WESTERN	\$0	\$0	\$0	\$100,000	\$100,000	\$166,095	\$33,905
(DR. V. PERCEC)							
UNC	\$0	\$0	\$0	\$150,000	\$150,000	\$282,580	\$37,420
(DR. E. T. SAMULSKI)							
DREXEL UNIV.	\$0	\$0	\$0	\$36,000	\$36,000	\$55,250	\$16,750
(DR. Y. WEI)							

BUDGET BALANCE
Carman/Hill

 \$747,605

[illegible]

DARPA/URI POLYMER PROGRAM REVIEW

January 14, 1992

subcontract to
UNIVERSITY OF PENNSYLVANIA
Contract No.: N00014-86-0766

Polymer Liquid Crystals

Participating Universities

Kent State University

J. W. Doane, Project Director
R. Gilpin
D. L. Johnson
A. Saupe
J. L. West

University of North Carolina

E. T. Samulski

Case Western Reserve University

V. Percec

II-B-203

*super technology
way of future*

RATIONALE

- Liquid crystals are a preferred technology for high definition television and other displays.
- Polymer liquid crystals and polymer dispersions give improved display characteristics
 - unlimited view angle
 - high contrast
 - high-brightness projection television *x 4-10 Brighter*
 - simplicity and lower cost *vs. tube.*
 - faster response *vs. crt.*
- Potential for new optical device products
 - switchable windows — *6 yrs ago - now commercial*
 - optical fiber crossbars
 - consumer products
 - IR modulation
- Potential for other products
 - high strength materials
 - nonlinear optical materials

*sun roofs - rear windows
in vans*

OBJECTIVES

- Synthesize innovative polymer liquid crystals for applications in:
 - electro-optic polymer dispersions
 - nonlinear optical materials
 - high strength materials
- Understand fundamental polymer and liquid crystalline properties:
 - electro-optic response
 - curvature elasticity/viscosity
 - dielectric properties
 - molecular ordering
 - surface and field effect
- Design new polymer dispersions for:
 - haze-free (wide angle) displays
 - reverse mode shutters
 - full color displays
 - low-power; low voltage electro-optic response



Summary of Program Findings:

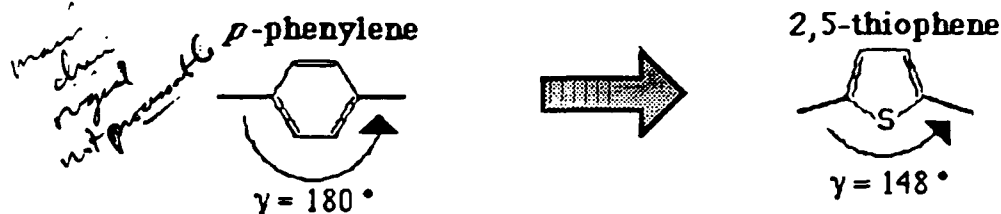
- New Thiophene-based, low-molar-mass and polymer liquid crystals have been discovered.
flexibility
- A model of flexible liquid crystals has been developed and applied to predict mesomorphism.
- NLO active polypeptides have been prepared.

Tangible Results:

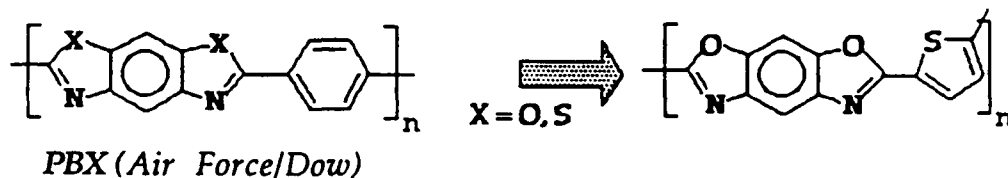
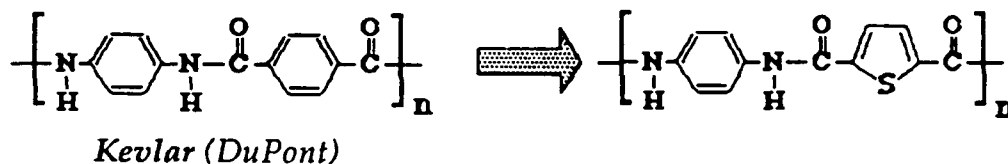
- In 1992 an industrial consortium will be established at UNC to study thiophene in high performance polymers.
- ONR will fund basic studies of thiophene-based polymers (1/92).
- Air Force funding of NLO polypeptides has commenced (5/91).

Technical Synopsis:

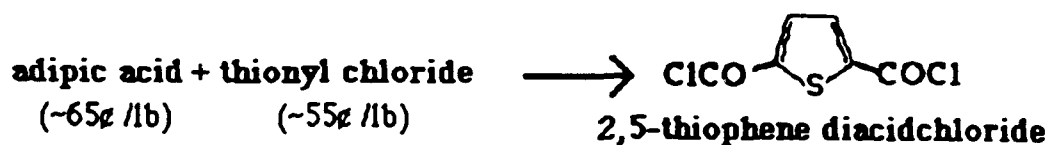
- Replacing *p*-phenylene with 2,5-thiophene introduces nonlinearity into polymer chains with retention of liquid crystallinity:



- We have succeeded in preparing thiophene-based analogs of ultra-high strength LCPs:



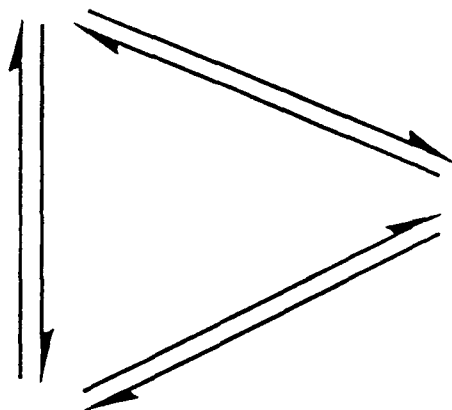
- The substitution is economically feasible: The diacidchloride may be prepared from readily available, inexpensive, bulk chemicals.



SIDE CHAIN LIQUID CRYSTALLINE POLYMERS

Virgil Percec, Case Western Reserve University

MOLECULAR UNDERSTANDING



MOLECULAR ENGINEERING

"potential applications"

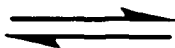
APPLICATIONS

- ANISOTROPIC GLASSES
- SELECTIVE WAVELENGTH DETECTORS
- POLARIZABLE FILTERS
- LARGE LC DISPLAYS
- INFORMATION STORAGE
- FERROELECTRIC MATERIALS
- PIEZOELECTRIC ELASTOMERS
- NON-LINEAR OPTICS
- INTEGRATED OPTICS
- DETECTORS & SENSORS
- SUPER-IONIC CONDUCTORS
- CHROMATOGRAPHIC STATIONARY PHASES
- PHOTOCHROMIC & PHOTO-CONDUCTIVE POLYMERS
- SUPERBARRIERS
- HIGH PERMEABILITY & SELECTIVITY MEMBRANES
- CONTROLLED DRUG RELEASE
- EXTERNALLY REGULATED SYSTEMS

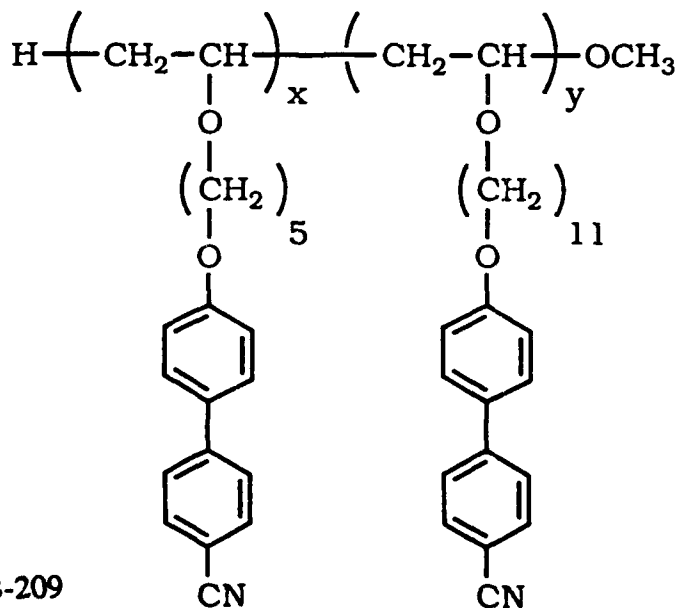
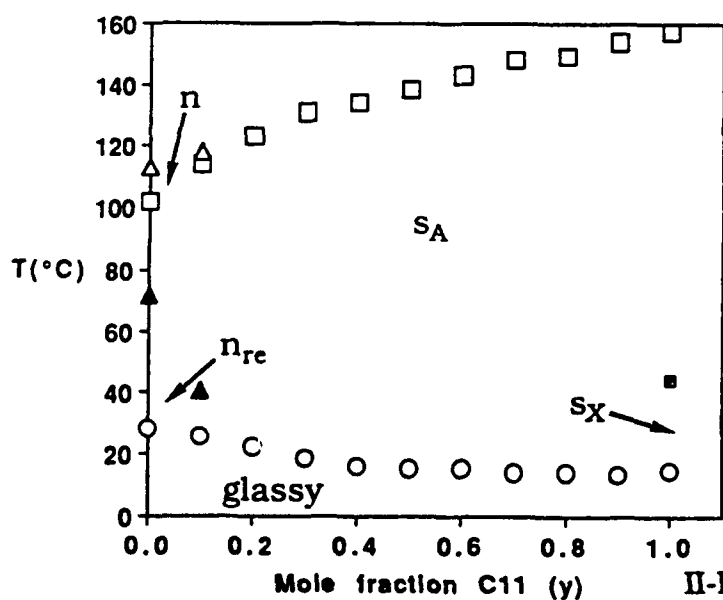
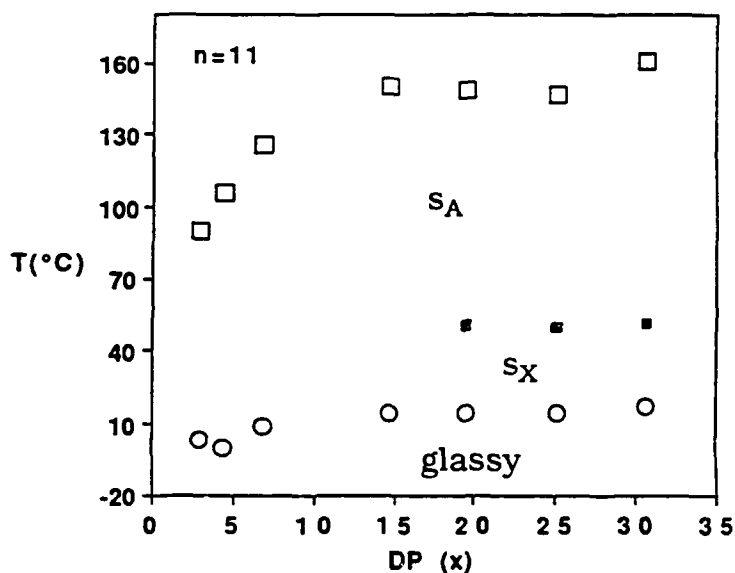
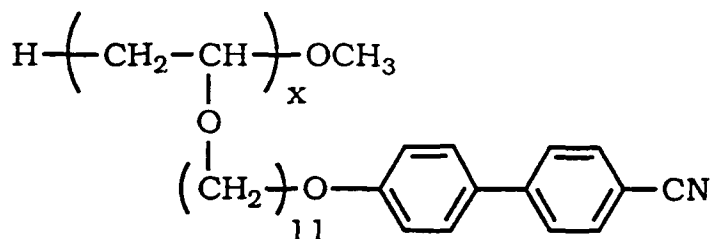
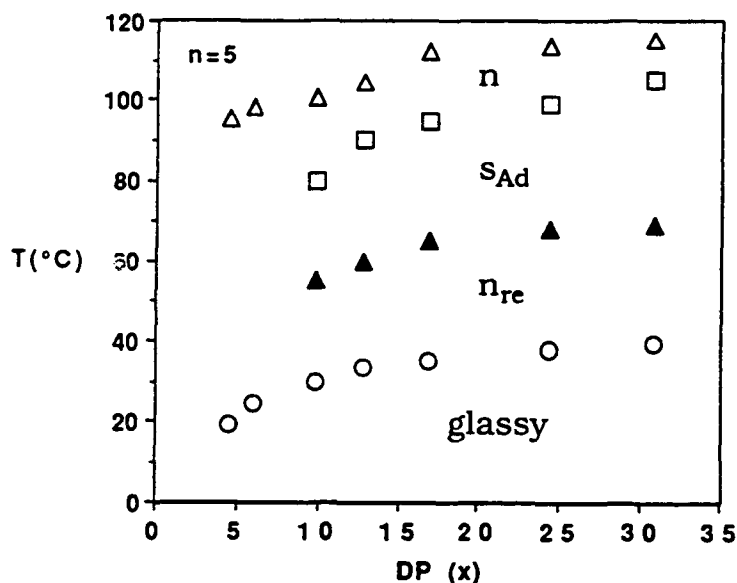
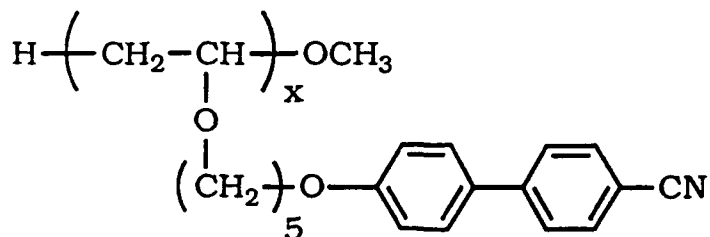
MOLECULAR ENGINEERING OF SIDE-CHAIN LIQUID CRYSTALLINE POLYMERS

n , S_A and n_{re}

Control of molecular weight, polydispersity and microstructure by living cationic polymerization of mesogenic vinyl ethers



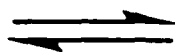
Molecular Understanding and Engineering of LCP Mesophases, Dynamics and Properties



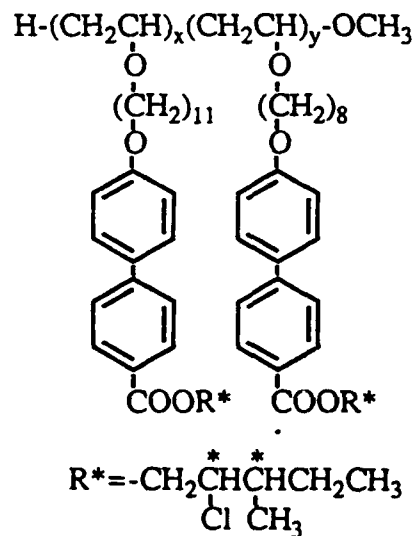
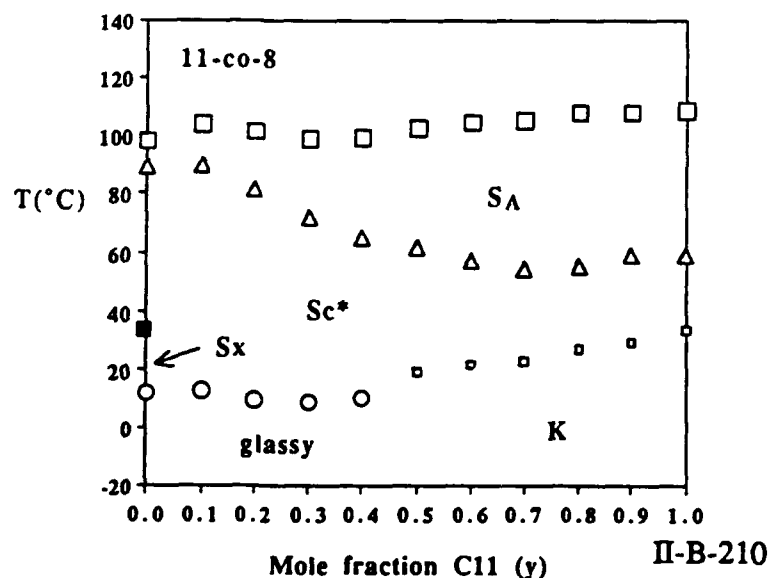
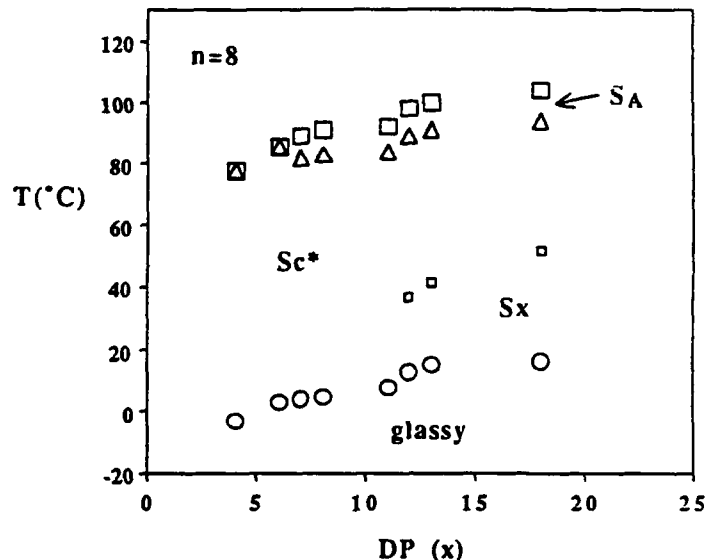
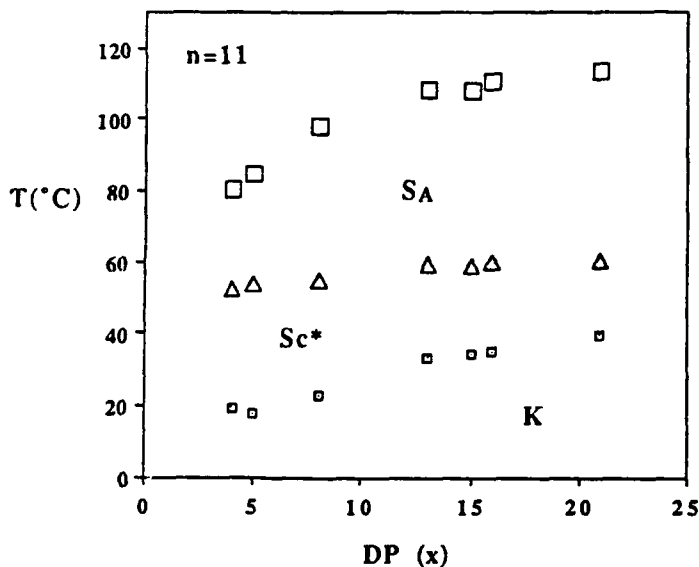
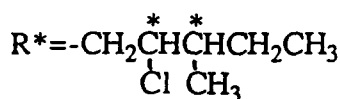
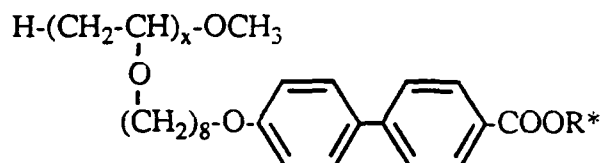
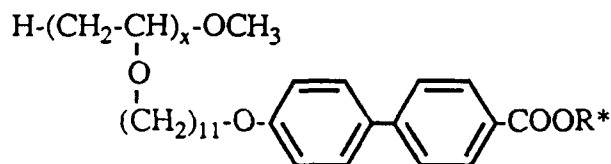
MOLECULAR ENGINEERING OF SIDE-CHAIN LIQUID CRYSTALLINE POLYMERS

s_A and s_c^*

Control of molecular weight,
polydispersity and microstructure
by living cationic polymerization
of mesogenic vinyl ethers



Molecular Understanding and
Engineering of LCP Mesophases,
Dynamics and Properties



CONCLUSIONS

Living cationic polymerization of mesogenic vinyl ethers provided the first series of quantitative information on the phase behavior of both side chain LC homopolymers and copolymers.

As predicted by thermodynamics (Percec and Keller, *Macromolecules*, **23**, 4347(1990)), the nature, number and temperature transitions of phase transitions of homopolymers are molecular weight dependent. For a certain polymer backbone, this dependence is dictated by the spacer length.

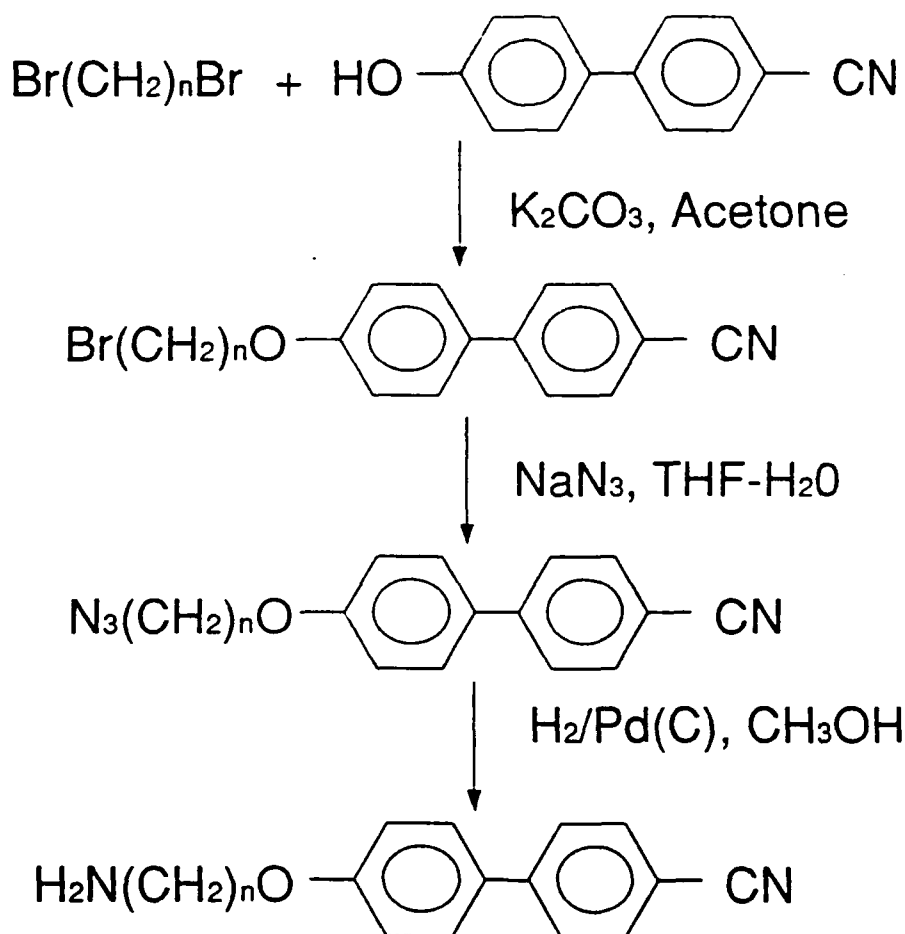
At constant molecular weight, the phase behavior of binary copolymers resembles that of an ideal solution derived from the structural units of the parent homopolymers. Phase transition temperatures and thermodynamic parameters of isomorphic structural units can be calculated by the Schroeder-Van Laar equation.

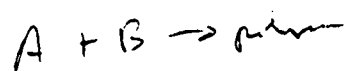
So far, living cationic polymerization and copolymerization were used to tailor make polymers with well-defined molecular weight, polydispersity, composition and chain ends, exhibiting nematic uniaxial (N_u), nematic reentrant (N_{re}), smectic A (s_A) and chiral smectic C (s_C^*) mesophases.

These results provide access to a quantitative manipulation of dynamics and properties of side chain liquid crystalline polymers which are requested for applications summarized in the introductory viewgraph.

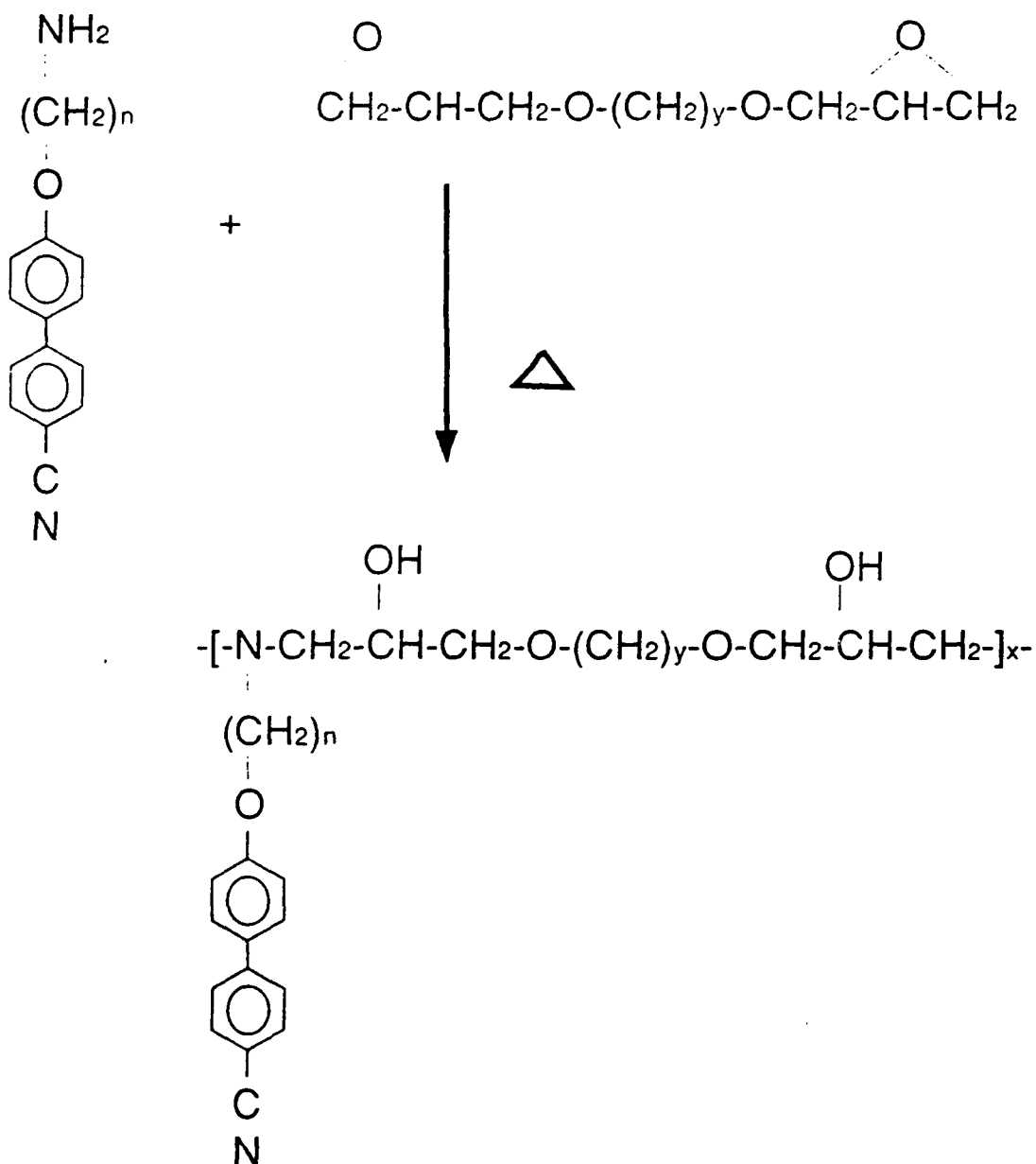
Synthesis of Mesogenic Alkyl Amines

L.C. Chien





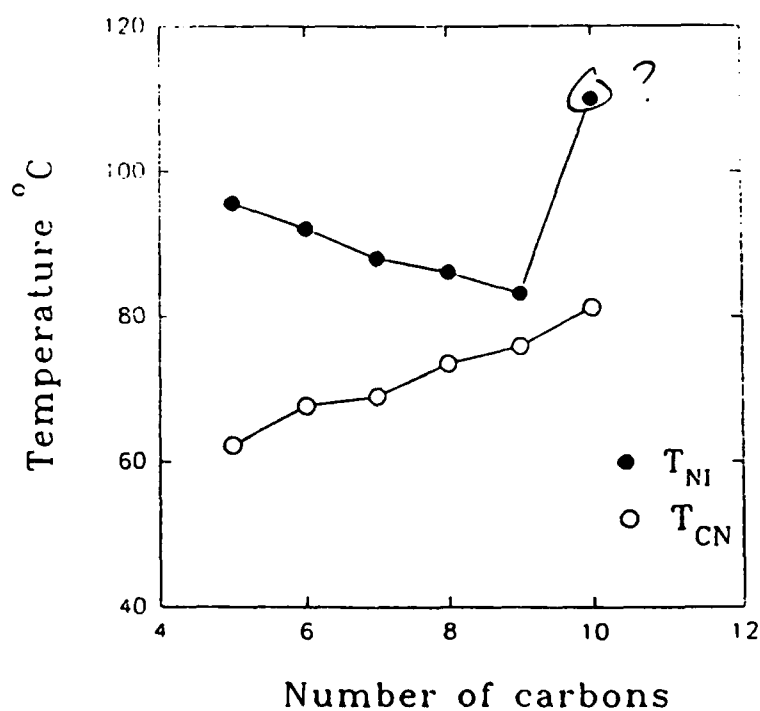
Synthesis of Side Chain Liquid Crystal Epoxies



II-B-213

Thermal Characteristics of Liquid Crystal Epoxies

amine (3)	n	$T_{CN}/^{\circ}C$	$\frac{\Delta H_m}{cal \cdot g^{-1}}$	$T_{NI}/^{\circ}C$	$\frac{\Delta H_i}{cal \cdot g^{-1}}$
a	5	62.16	15.48	95.59	0.47
b	6	67.67	8.36	92.14	0.15
c	7	69.02	16.43	87.99	0.59
d	8	73.48	19.41	86.08	0.55
e	9	75.89	23.8	83.18	0.59
f	10	81.24	19.06	110.04	0.27



II-B-214

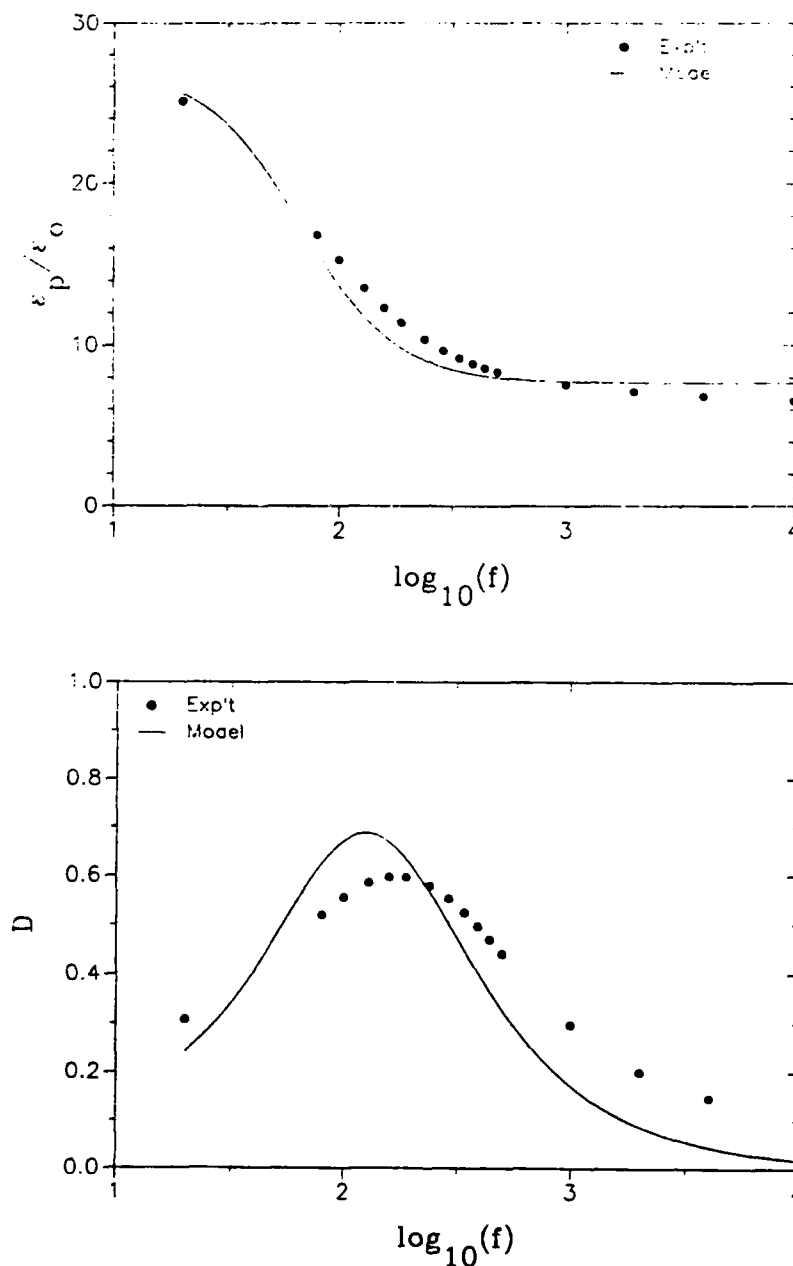
Dielectric Response of PDLC Films

Jack Kelly

- Studied the dielectric properties of PDLCs as a function of frequency (0.1–100kHz) and temperature (-10°C to 100°C)
- Motivation: Dielectric properties contribute to the electro-optic response (i.e., the field in a droplet)
- Systems studied:
 1. Thermally cured epoxies
 2. UV cured epoxies
 3. Thermoplastic (PMMA)
- Major effects observed in the response
 1. Plasticization of the polymer by liquid crystal in the matrix
 2. Ionic charge accumulation at the liquid crystal/polymer interface
- Developed a model that predicts main features of the dielectric response
 - Self-consistent field approach
 - Complex dielectric constant: $\epsilon + i\frac{g}{\omega}$
 - Predicts the dielectric constant and the dissipation
- Correlation of the dielectric response with electro-optic response
 - Shielding of the applied field at low frequencies
 - Charge depletion in the droplets
 1. saturation of the shielding
 2. shielding strongly dependent on droplet size

Dielectric Response of PDLC Films

Jack Kelly

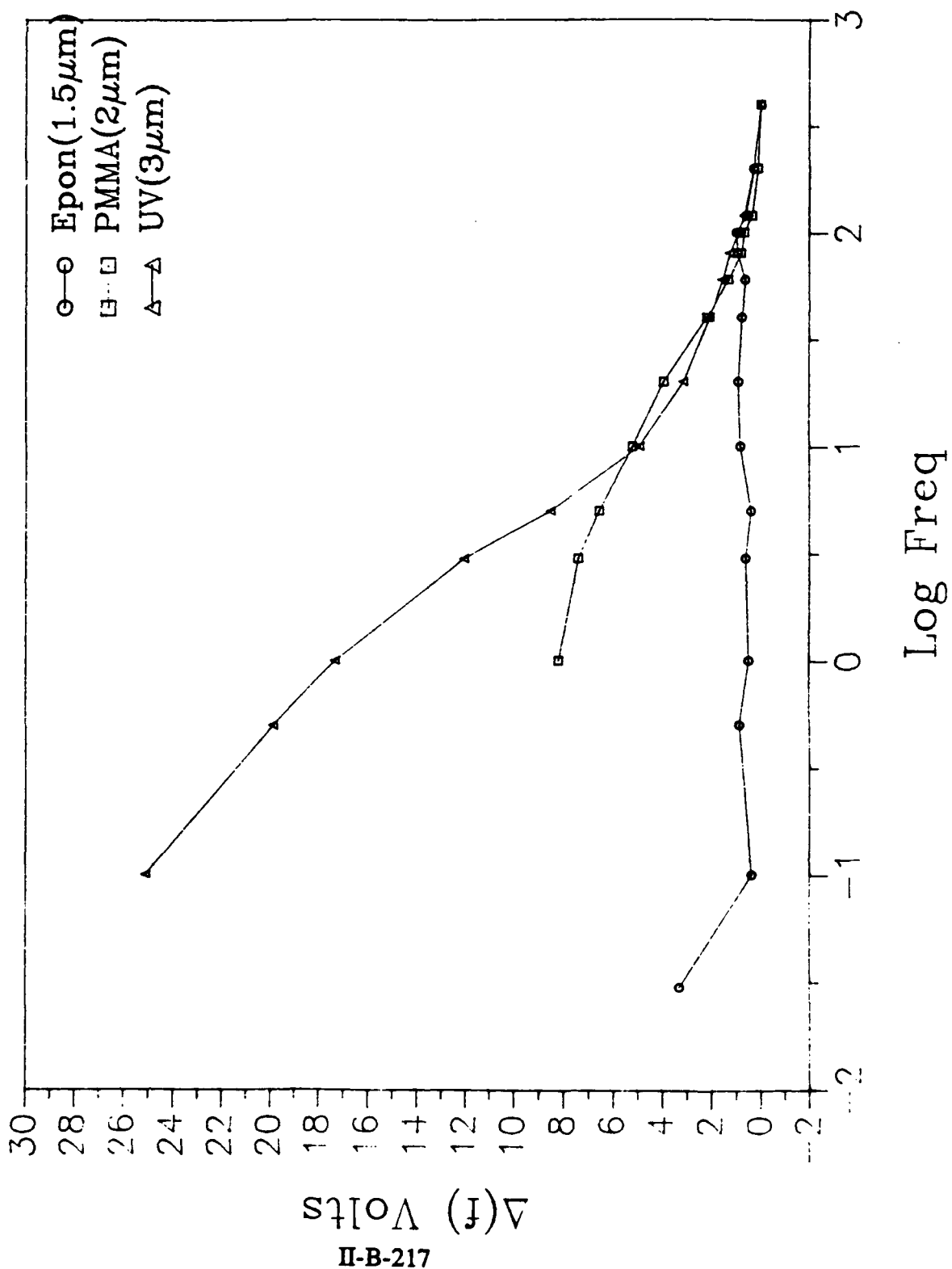


Plots of the relative dielectric constant and dissipation factor as a function of frequency. The model presumes the only dissipative mechanism is conduction. The conductivity of the droplet was three orders of magnitude greater than the polymer to achieve the fit.

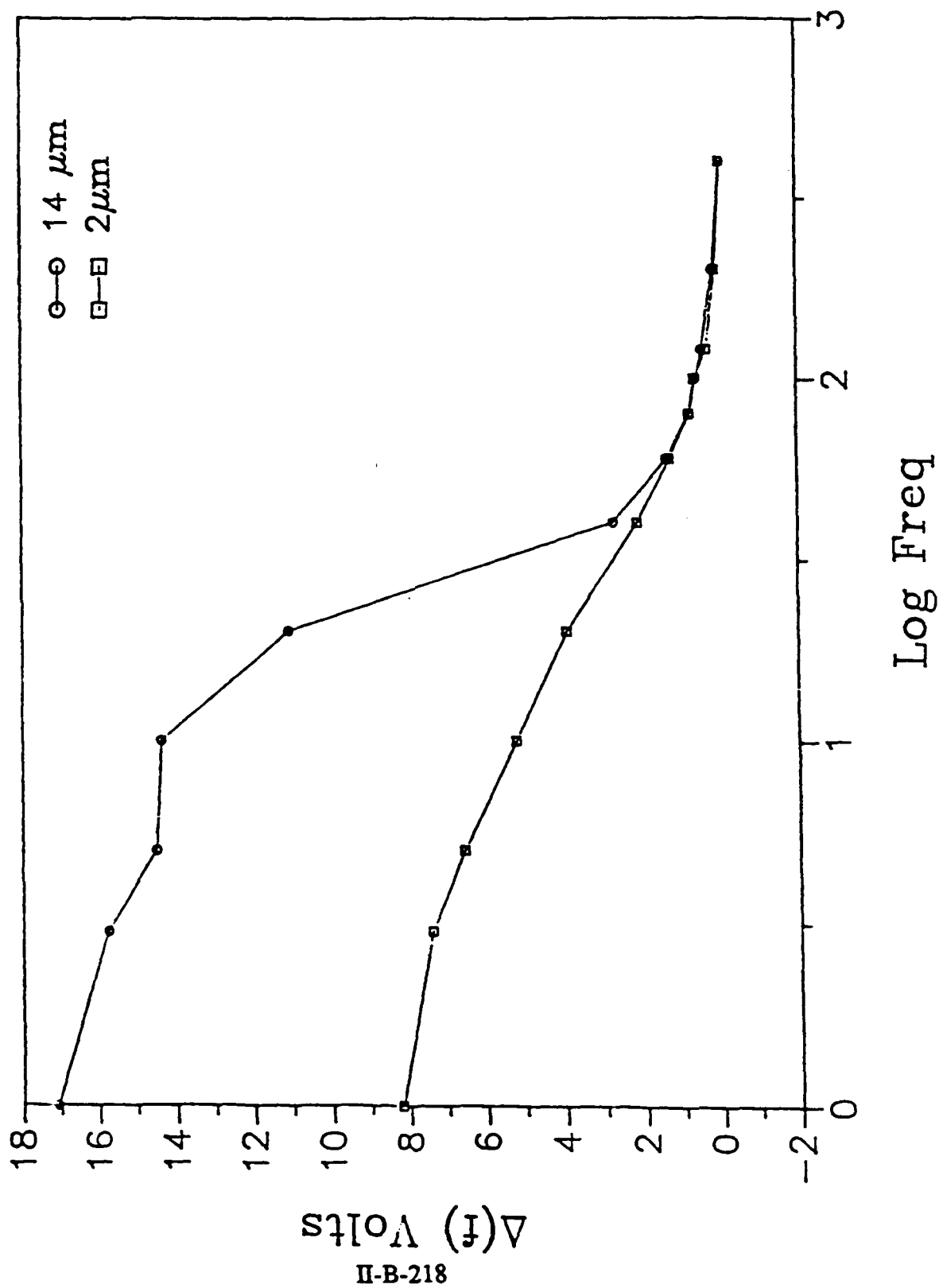
II-B-216

LCI
Kent State University

Shielding for three types of film



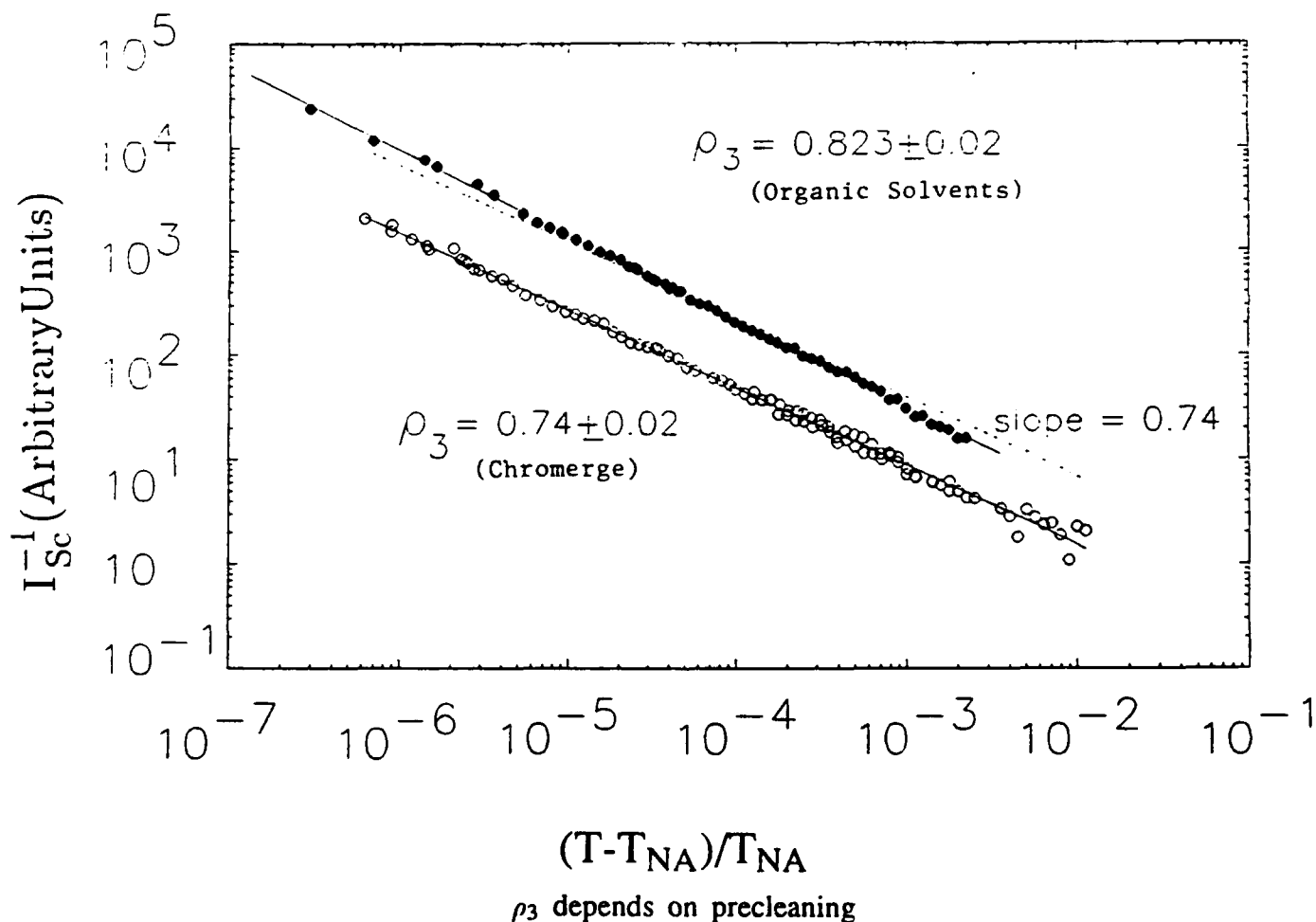
Shielding for two droplet sizes of a PDLC film



Nematic Smectic A Criticality: Surface Anchoring Effects

David L. Johnson

- K_{33} diverges at T_{NA} : $\rho_3 \equiv$ Critical Exponent
- $I_{Sc}^{-1} \sim K_{33} \sim (T-T_{NA})^{-\rho_3}$



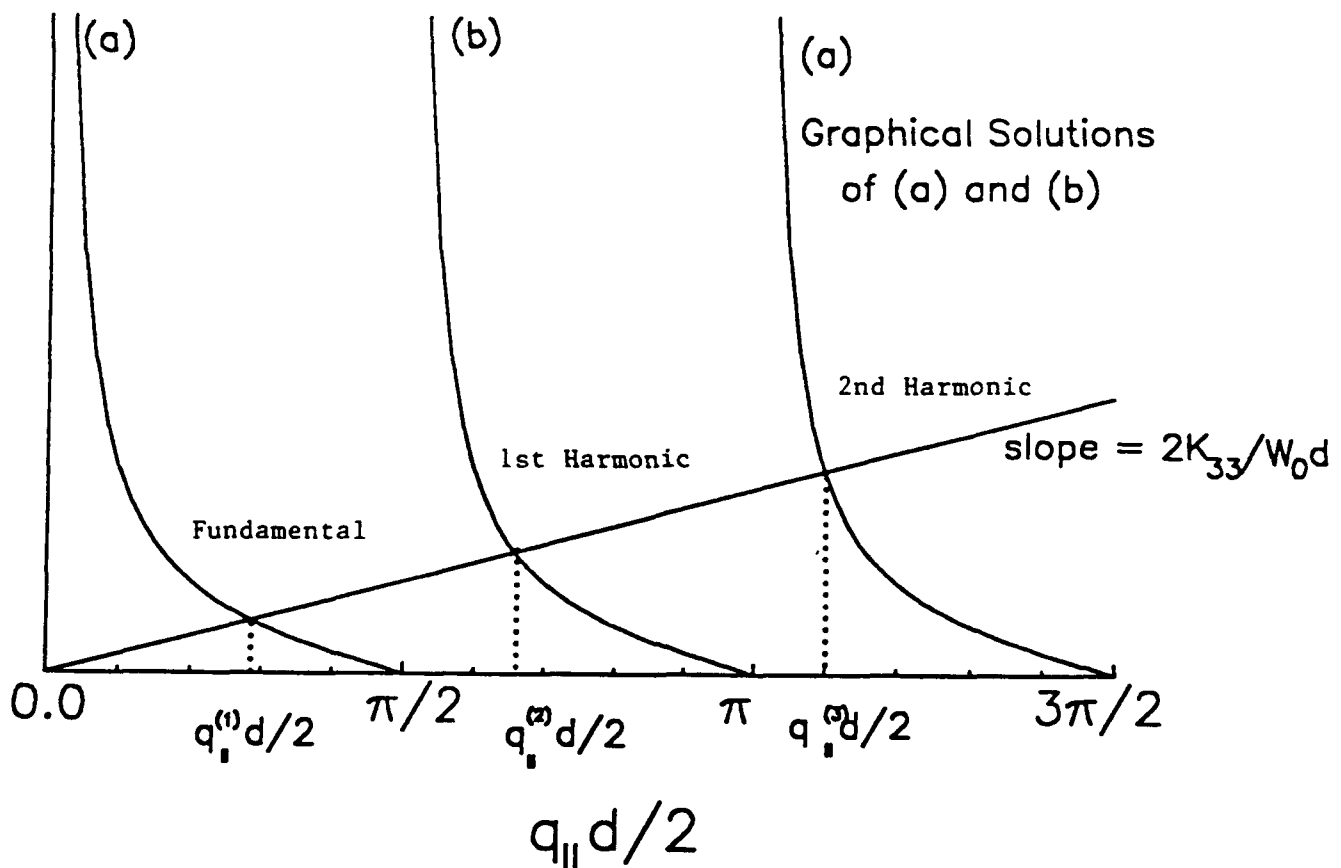
II-B-219

Director Mode Shift Due to Finite Anchoring

- Homeotropic Alignment (silane)
- Director Normal Modes are solutions of:

$$\frac{2K_{33}}{W_0 d} (q_{||} d/2) = \cot(q_{||} d/2) \dots \dots \dots (a)$$

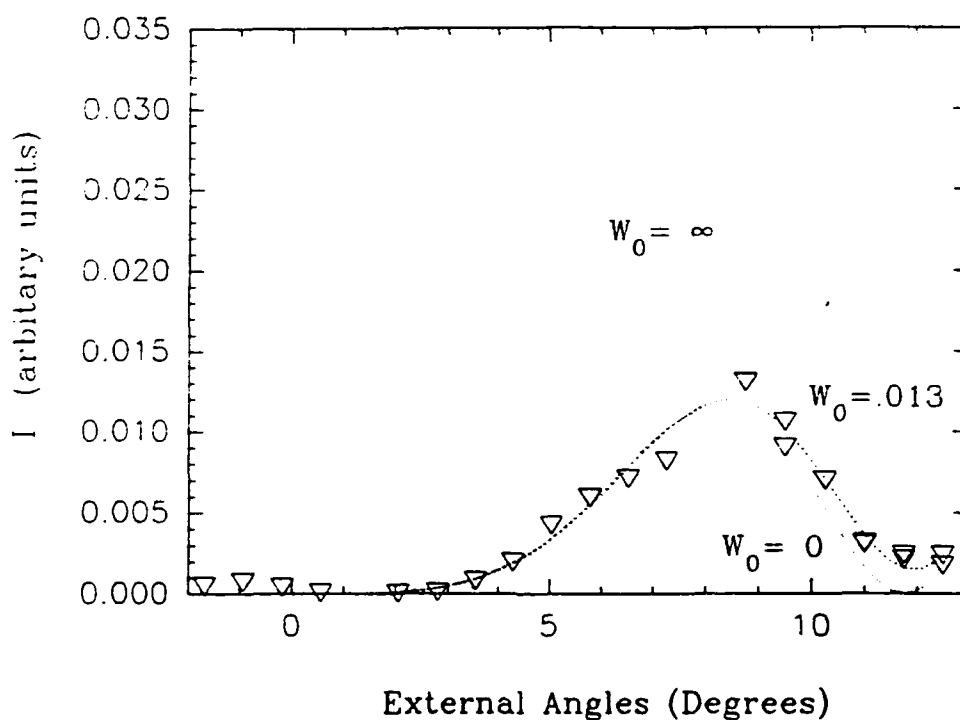
$$\frac{2K_{33}}{W_0 d} (q_{||} d/2) = -\tan(q_{||} d/2) \dots \dots \dots (b)$$



II-B-220

Angular Dependence of Fundamental Mode Light Scattering

- $I_{sc}(0)$ depends on W_0 and K_{33} separately
- $T - T_{NA} = 0.010K$: K_{33} is large ($\sim 10^{-5}$ dynes)
- $W_0 \sim 0.013 \text{ erg/cm}^2$

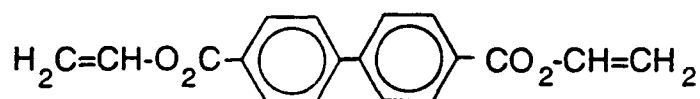


- New and Efficient Method for Measuring W_0 and K_{33}
- Exactly analogous experiments measure K_{22} , K_{11} , W_i (either of two inpl anchoring coefficients)

New work

Polymer Gel Dispersion

Gel Monomer:



Dispersion Preparation:

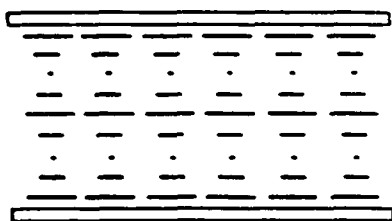
- Dissolve ~2% monomer in liquid crystal
- Achieve desired alignment of liquid crystal
 - applied field
 - surface
- Photopolymerize to form gel

II-B-222

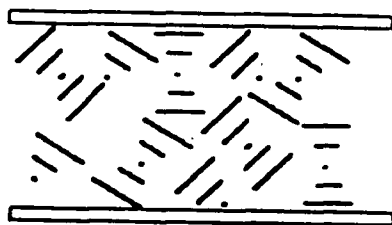
Chiral Nematic Textures

Texture

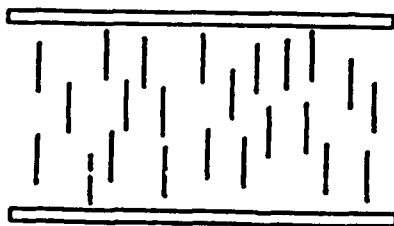
Planar (Grandjean)



Focal Conic



Homeotropic



Electric Field

Strength

$E=0$

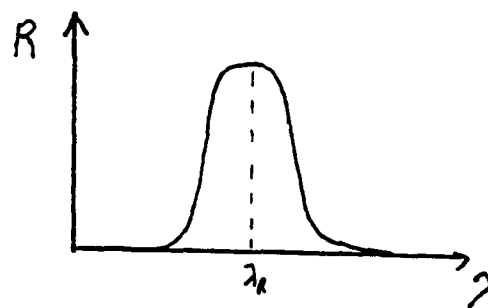
$E < E_c$

$E > E_c$

II-B-223

Optical State

Bragg Reflection



Scattering

Transparent

LCI

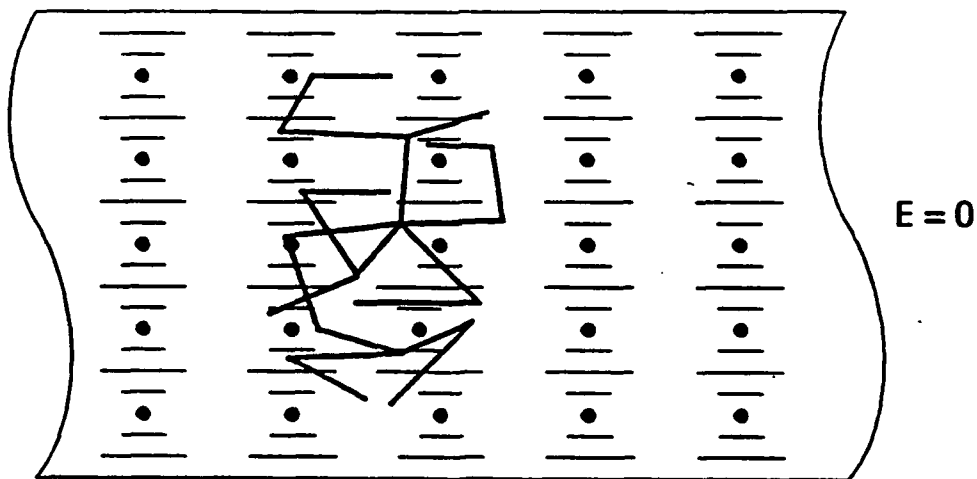
Kent State University

Reverse Mode Shutter

Aligned State:

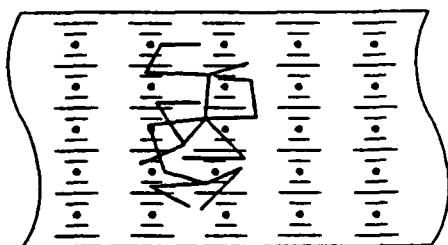
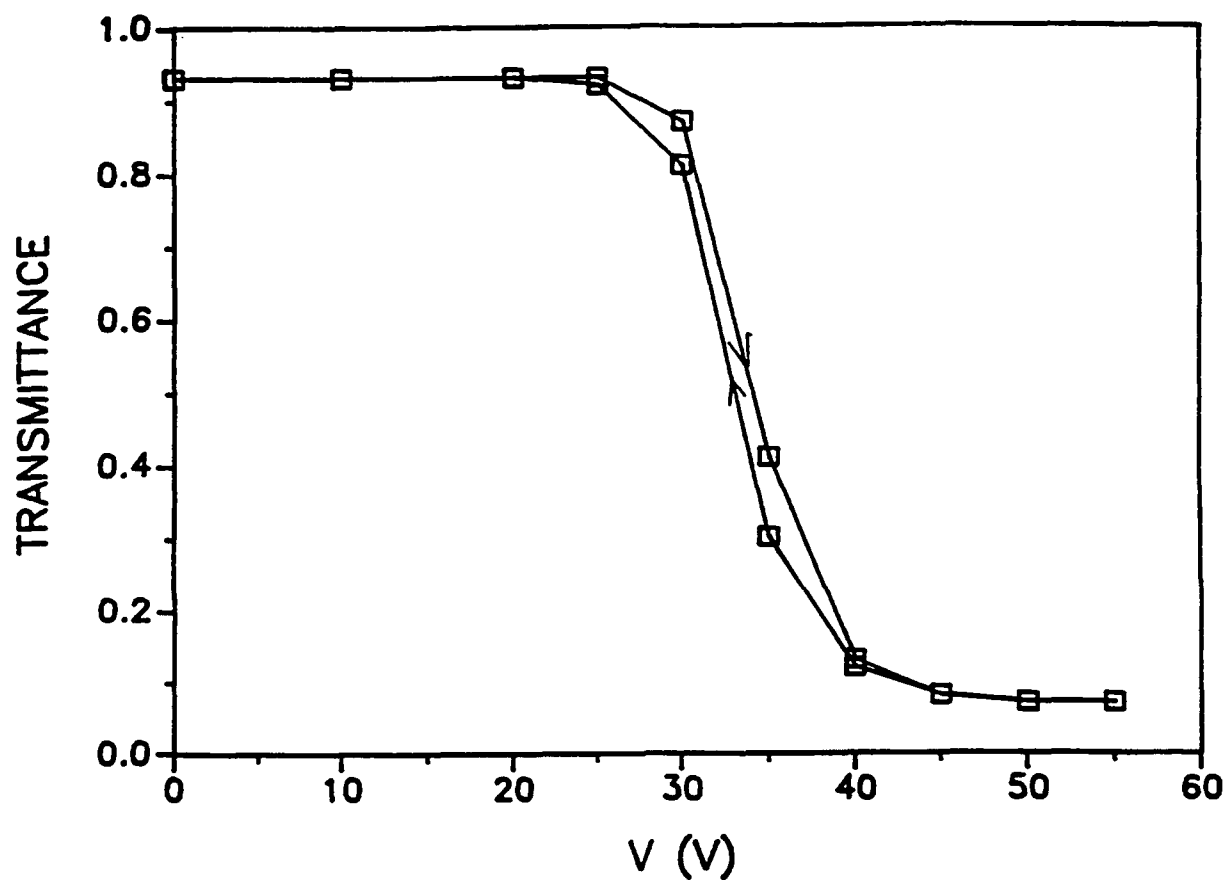
- chiral nematic planar texture
- pitch length $\simeq 4.0 \mu\text{m}$ (infrared)

Model network following polymerization

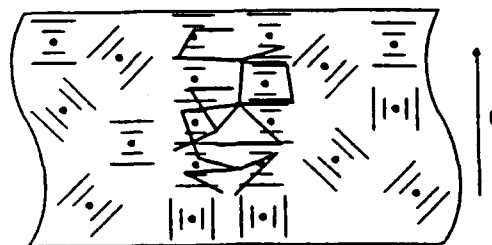


II-B-224

Reverse Mode Response



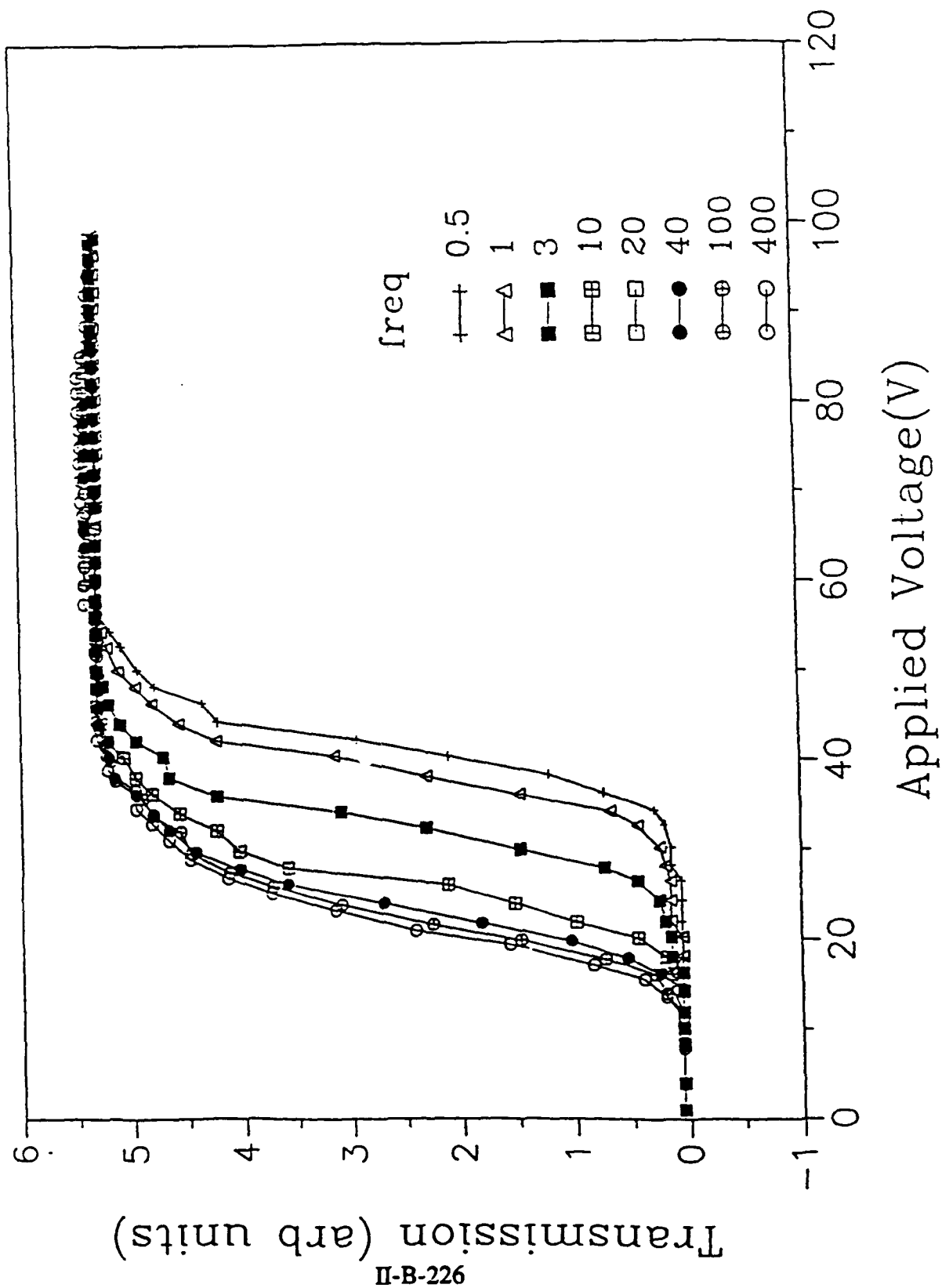
Clear State



Scattering State

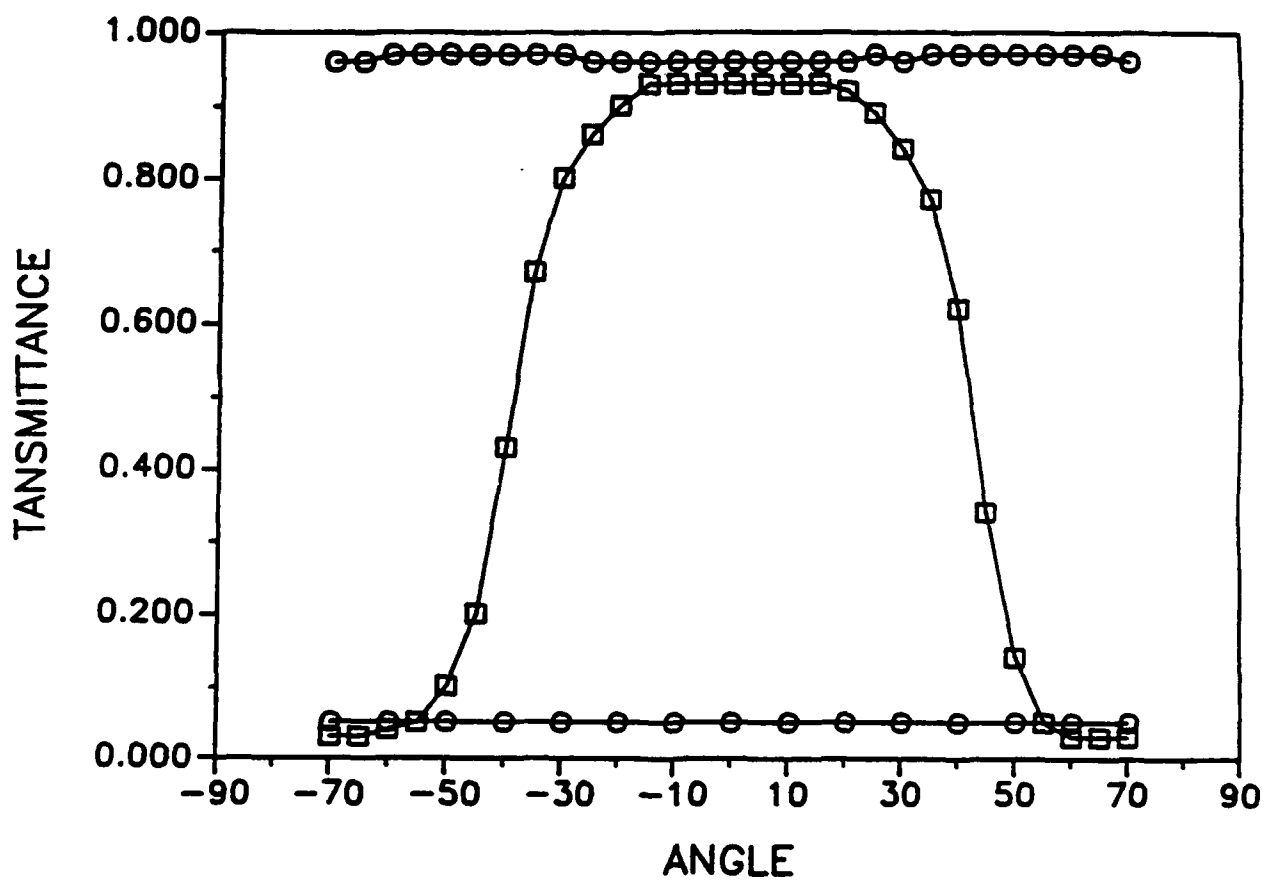
II-B-225

Optical Transmission vs Applied Field



Haze-Free Feature

Angular dependence of transmission



- - PDLC with isotropic polymer binder
- - Gel dispersion

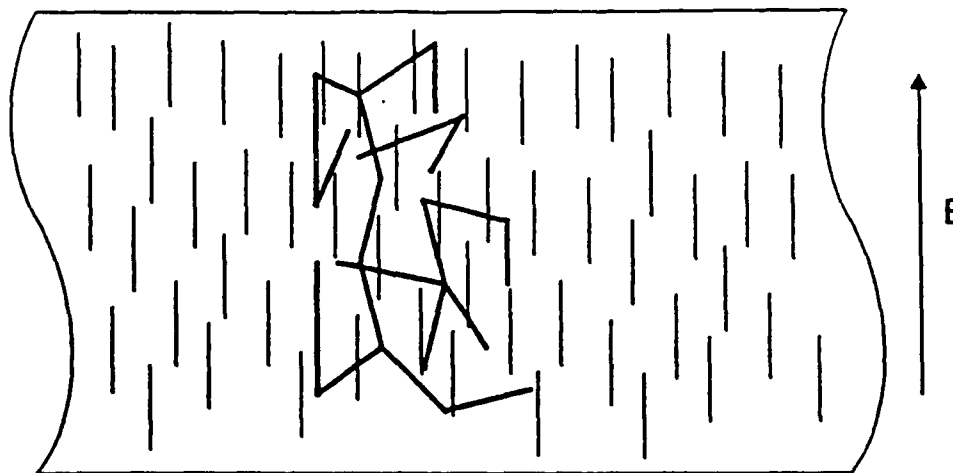
II-B-227

Normal Mode Shutter

Aligned State:

- homeotropic alignment under applied field

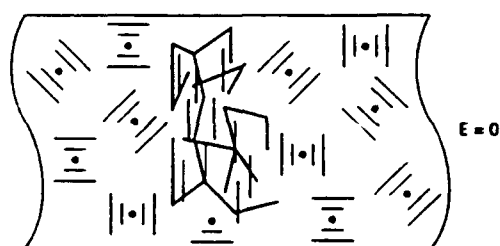
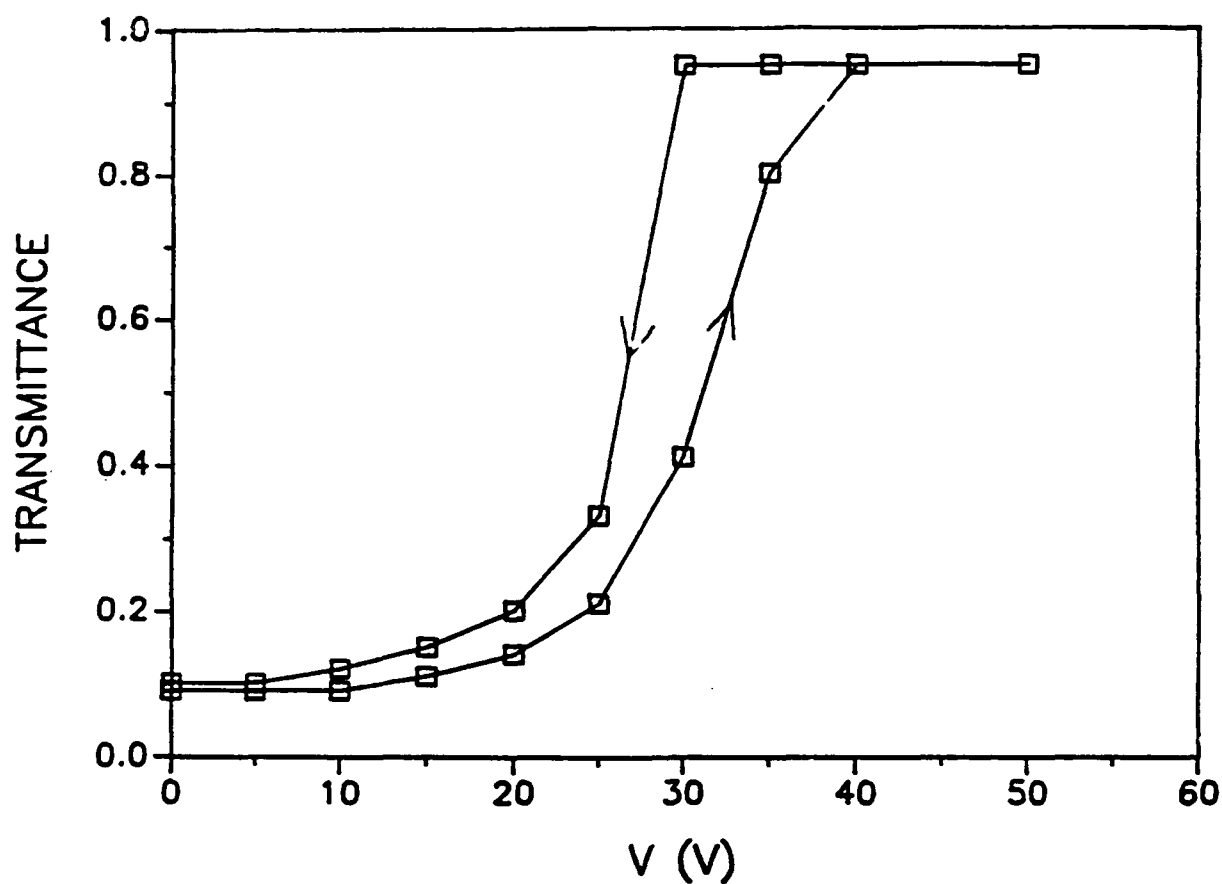
Model network following polymerization



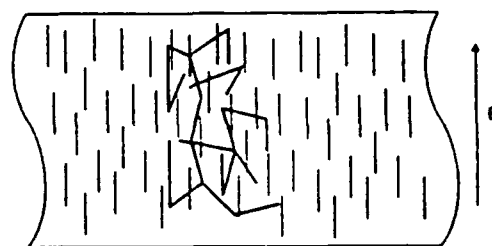
Polymerize in aligned state

II-B-228

Response to Continuous Voltage (2 kHz)



Scattering State



Clear State

II-B-229

URI Related Projects

<u>Grant</u>	<u>Agency</u>	<u>Amount</u>
URI	DARPA 9/86 Navy N0014-86-K-0772	\$815K
URI	DARPA 10/89 Navy N0014-86K-0766	\$700K
NCIPT (USC, UCLA, MIT, Columbia)	DARPA 3/90 MDA972-90-C-0037	\$1.2M
HDDT	DARPA 1/91 N00014-90-J-1559	\$227K
ALCOM (Case Western Reserve, University of Akron)	NSF 2/91 DMR-8920147 Ohio	\$18M est.
HDDT	DARPA 9/91 MDA-972-91-J-1020	\$1.2M

APPENDIX I

PUBLICATIONS/PATENTS

April 1, 1990 — September 30, 1991

Contract No. N00014-86-K-0766

Kent State University
University of North Carolina

Papers Submitted to Refereed Journals but not published.

M. Jaroniec, S. Lin, R.K. Gilpin, "Use of a Displacement Model for Solvent Sorption to Study Non-Specific Selectivity in Reversed-Phase Liquid Chromatography," *Chromatographia*, submitted 1991.

M. Jaroniec and R.K. Gilpin, "Theory of Liquid-Solid Adsorption Chromatography with Mixed Eluents on Energetically Heterogeneous Adsorbents," *Langmuir*, in press 1991.

R. Ondris-Crawford, E.P. Boyko, B.G. Wagner, J.H. Erdmann, S. Žumer and J.W. Doane, "Microscope Textures of Nematic Droplets in Polymer Dispersed Liquid Crystals," *J. Appl. Phys.*, (to appear).

C. Lin and L.-C. Chien, "Synthesis and Characterization of Side-Chain Liquid Crystalline Epoxy Polymers," *Macromolecules*, submitted 1990.

J.L. West and R. Ondris-Crawford, "Characterization of Polymer Dispersed Liquid Crystal Shutters by UV and IR Absorption Spectroscopy," *J. Appl. Phys.*, submitted 1991.

Papers Published in Refereed Journals

L.C. Chien and C. Lin, "Side Chain Liquid Crystal Epoxy Polymers," *Polymer Preprints*, 30(2), 665 (1990).

R.K. Gilpin, M. Jaroniec and M.B. Martin-Hopkins, "Use of a Gamma Energy Distribution to Model the Gas Chromatographic Temperature Dependence of Solute Retention on Aryl-Siloxane Chemically Modified Porous Carbon," *J. Chromatogr.* 513, 1 (1990).

R.K. Gilpin, M. Jaroniec and S. Lin, "Characterization of the Surface Composition of Alkyl Bonded Phases Under Reversed-Phase Liquid Chromatographic Conditions Using Homologs of Alkanoate and Perfluoroalkanoate Esters as Solute Probes," *Anal. Chem.* 62, 2092 (1990).

R.K. Gilpin, M. Jaroniec and S. Lin, "Dependence of Methylene Selectivity on the Composition of Hydro-Organic Eluents for Reversed-Phase Liquid Chromatographic Systems with Alkyl Bonded Phases," *Chromatographia* 30, 393 (1990).

L.C. Chien, "Epoxyes for High-Definition Displays," *Innovations in Polymers/Engineering Plastics* 1, November (1990).

A. Jáklí, D.R. Kim, M.R. Kuzma and A. Saupe, "Rotational Viscosities of Polymer Solutions in a Low Molecular Weight Nematic Liquid Crystal," *Mol. Cryst. Liq. Cryst.* 198, 331 (1991).

A. Jáklí and A. Saupe, "Linear Electromechanical Effect in a S^{*}C Polymer Liquid Crystal," *Liquid Crystals* 9(4), 519 (1991).

J.W. Doane, J.L. West, J.B. Whitehead, Jr. and D.S. Fredley, "Wide-Angle View PDLC Displays," *SID Digest* XXI 224 (1990).

J.H. Erdmann, B.G. Wagner, G.P. Crawford, S. Žumer and J.W. Doane, "Director Configuration Transitions in PDLC Materials," *Liquid Crystal Displays and Applications*, SPIE 1257, 68 (1990), ed. J.W. Doane.

J.W. Doane, "Polymer-Dispersed Liquid Crystals: Boojums at Work," *MRS Bulletin* XVI, 22 (1991).

R. Ondris-Crawford, E.P. Boyko, G.P. Crawford and J.W. Doane, "Molecular Anchoring at the Droplet Wall in PDLC Materials," *Proceedings of SPIE*, 1244, (1991).

J.L. West and D.S. Fredley, "Electro-optics of Polymer Dispersed Liquid Crystals Utilizing Birefringent Binders," *Proceedings of SPIE*, 1244, (1991).

D. Seekola and J. Kelly, "A Comparative Study of the Dielectric and Optical Response of PDLC Films," *Proceedings of SPIE*, 1244, (1991).

L.C. Chien and C. Lin, "Synthesis and Structure Property Relations of Liquid Crystalline Epoxy Polymers," *Proceedings of SPIE*, 1244, (1991).

M.B. Martin-Hopkins, R.K. Gilpin and M. Jaroniec, "Studies of the Surface Heterogeneity of Chemically Modified Porous Carbons by Gas-Solid Chromatography," *J. Chromatogr. Sci.* 29, 147 (1991).

Books and Chapters Submitted but not yet Published

None

Books or Chapters Published

J.L. West in "Polymer Dispersed Liquid Crystals," *Liquid Crystalloid Polymers*, eds.: R.A. Weiss and C.K. Ober, ACS Symposium Series 435 (1990), p. 475-495.

J.W. Doane, "Polymer Dispersed Liquid Crystal Displays" in *Liquid Crystals, Applications and Uses*, ed.: B. Bahadur, World Scientific Publishing, Singapore, (1990), p. 361-395.

Patents Filed

J.L. West and J.W. Doane, "Infrared Light Modulating Material Comprising a Liquid Crystal and a Medium," Appl. #07/582,239, filed May 1991.

J.W. Doane, D.K. Yang and L.C. Chien, "Liquid Crystalline Light Modulating Device and Material," Appl. #07/694,840, filed May 1991.

Patents Granted

J.W. Doane and J.L. West, "Light Modulating Materials Comprising a Liquid Crystal Phase Dispersed in a Birefringent Polymeric Phase," U.S. Patent No. 4,994,204, issued February 19, 1991.

J.L. West, "Extended Temperature Range PDLC Shutters," U.S. Patent No. 5,004,323, issued April 2, 1991.

J.L. West, "Novel Cyanobiphenyl Amines and Liquid-Crystalline-Side-Group Polymers Incorporating Same," Appl. #07/447,582, issued May 15, 1991.

APPENDIX II

**INVITED/CONTRIBUTED PRESENTATIONS
HONORS/AWARDS/PRIZES**

April 1, 1990 — September 30, 1991

Contract No. N00014-86-K-0766

**Kent State University
University of North Carolina**

Invited Presentations at Workshops or Professional Society Meetings

J.L. West, "Polymer Dispersed Liquid Crystals: New Developments," Ohio Academy of Science, Ohio State University, April 26, 1991.

A. Saupe and J. Liu, "Biaxial Nematics," Ohio Academy of Science, Ohio State University, April 26, 1991.

Presentations at Workshops or Professional Society Meetings

J.L. West, D.S. Fredley and L.-C. Chien, "Liquid Crystal Epoxies for Use in Haze-Free Polymer Dispersed Liquid Crystals," 13th International Liquid Crystal Conference, Vancouver, July 1990.

R.J. Ondris, J.L. West and J.W. McCargar, "Dichroic Measurements in the Infrared of Cyanobiphenyl Liquid Crystal Mixtures," 13th International Liquid Crystal Conference, Vancouver, July 1990.

L.-C. Chien, D.S. Fredley and J.L. West, "Synthesis of Mesogenic Curing Agents for the Preparation of Liquid Crystal Epoxies," 13th International Liquid Crystal Conference, Vancouver, July 1990.

J.L. West, D.S. Fredley and J.W. Doane, "Formation of Haze-Free Polymer Dispersed Liquid Crystals (PDLC)," 13th International Liquid Crystal Conference, Vancouver, July 1990.

J.W. Doane, G.P. Crawford and D.K. Yang, "NMR of Surfaces and Confinement Effects on Liquid Crystals," American Chemical Society, Cleveland, September 1990.

R.K. Gilpin, L.J. Wu and M.E. Gangoda, "The Application of Fluorinated Modifiers to Enhance Performance in HPLC," 42nd Pittsburgh Conference, Chicago, March 1991.

J.W. Doane, "Polymer Dispersed LCDs," Flat Panel Field Day, New York, 1990.

R.K. Gilpin and M.E. Gangoda, "Use of Fluorinated Compounds as Additives in HPLC," 17th FACSS Meetings, Cleveland, Ohio, October 1990.

M.E. Gangoda and R.K. Gilpin, "²H-NMR Studies of Structural Dynamics of Alkyl Modified Silica," 17th FACSS Meeting, Cleveland, Ohio, October 1990.

S. Lin and R.K. Gilpin, "Chromatographic and NMR Studies of the Interfacial Solvent Composition of Bonded Phases," 17th FACSS Meeting, Cleveland, Ohio, October 1990.

P. Kasturi and R.K. Gilpin, "Reordering/Resolution of Chemically Modified Alkyl Surface Using High Aqueous Mobile Phases," 17th FACSS Meeting, Cleveland, Ohio, October 1990.

R. Ondris-Crawford, E.P. Boyko, G.P. Crawford and J.W. Doane, "Molecular Anchoring at the Droplet Wall in PDLC Materials," SPIE/IS&T Symposium on Electronic Imaging Science and Technology, San Jose, CA, February 24-March 1, 1991.

J.L. West and D.S. Fredley, "Electro-optics of Polymer Dispersed Liquid Crystals Utilizing Birefringent Binders," SPIE/IS&T Symposium on Electronic Imaging Science and Technology, San Jose, CA, February 24-March 1, 1991.

D. Seekola and J. Kelly, "A Comparative Study of the Dielectric and Optical Response of PDLC Films," SPIE/IS&T Symposium on Electronic Imaging Science and Technology, San Jose, CA, February 24-March 1, 1991.

L.C. Chien and C. Lin, "Synthesis and Structure Property Relations of Liquid Crystalline Epoxy Polymers," SPIE/IS&T Symposium on Electronic Imaging Science and Technology, San Jose, CA, February 24-March 1, 1991.

R.K. Gilpin, L.J. Wu and M.E. Gangoda, "The Application of Fluorinated Modifiers to Enhance Performance in HPLC," 42nd Pittsburgh Conference, Chicago, IL, March 1991.

P. Kasturi, L.J. Wu and R.K. Gilpin, "Reordering/Resolution Studies of the Interfacial Properties of Chemically Modified Alkyl Surfaces," 42nd Pittsburgh Conference, Chicago, IL, March 1991.

M.E. Gangoda and R.K. Gilpin, "Studies of the Interfacial Properties of Chemically Modified Silica by ^2H -NMR Spectrometry," 42nd Pittsburgh Conference, Chicago, IL, March 1991.

Honors/Awards/Prizes for Contract Employees

Dr. Antal Jáklí received the "1991 Provost's International Scholar Award" from Kent State University for exceptional scholarly productivity in the area of Physical Properties of Liquid Crystals.

APPENDIX III

INDUSTRIAL/ACADEMIC INTERACTIONS

April 1, 1990 — September 30, 1991

Contract No. N00014-86-K-0766

Kent State University
University of North Carolina

II-B-238

Visits By/To Industry and Commercialization

Date	Visitor	Address
1990		
July 20	Quinten Kroes	University of Twente, The Netherlands
July 23	Senri Miyaska Seiichi Arakawa	SONY Research Center
August 3	Jon Deex	Zero Corp.
August 3	Frank Allan	EM Industries, Hawthorne, NY
August 17	Dr. Kazutami Sakamoto	Ajinomoto Co., Teaneck, NJ
August 25	Dr. David Casasent Dr. Neil H. Carnob	Carnegie Mellon Univ., Pittsburgh, PA
September 28	Dr. Howard Mettee Dr. Duan F. Rost Dr. J.D. Bakos, Jr.	Youngstown State University, Youngstown, OH
October 10	John Carter	Goodyear
October 12	Mr. William Marks	BFGoodrich Aerospace
October 25	Dr. Dave Margerum	Hughes Research, Malibu, CA
December 13	Dr. J.C. Lee	Samsung, Sed, Korea
1991		
January 7	Dr. H. Hakemi	SNIA, BPA, Italy
January 30	Dr. Harvey Scher	BP Research, Cleveland, OH
February 18	Dr. Kris Baranwal	Uniroyal Goodrich, Akron, OH
March 4	Dr. Ulrich Finkenzeller	E Merck, Darmstadt, Germany
April 3	Gerry Brown	State University of NY, Stony Brook, NY
April 5	Dr. John Turn	Materials Research Labs, WPAFB
April 24	Jim Gray	Warner Cable, North Dublin, OH
April 26	Hahn Torn	Royal Institute of Technology, Sweden
May 13	Dr. Akihiro Mochizuki	Fujitsu Labs, Atsugi, Japan
May 14	14 Japanese Display Scientists led by Dr. S. Kobayashi - Dr. Yoshikazu Yabe Dr. Kumio Kihara Dr. Shoji Yamaguchi	Fujitsu Kiden Ltd. Mitsubishi Petrochemical Co.

May 29	James Stroh Jerry Arth	LXD, Inc., Oakwood, OH
June 3	Dr. W.J. Marks Dr. B.D. Desai Dr. John Taylor	BFGoodrich Aerospace Display, Hatfield, PA
June 14	Dr. K. Sakamoto Dr. K. Yamada Dr. T. Takahashi	Ajinomoto, Teaneck, NJ
June 14	Dr. Hundi P. Kamath Dr. Stephen Moore Dr. Phil Jones	Raychem Corp., Menlo Park, CA
June 14	Dr. David Coates	BDH
June 14	Dr. Bruce Nerad	3M, St. Paul, MN
June 14	Dr. Paul Drzaic	Taliq Corp., Sunnyvale, CA
June 14	Dr. B. Bahadur	Litton Data Images, Ottawa, Canada
June 14	Dr. H. Takatsu	Dainippon Ink & Chem., Japan
June 14	Dr. David Margerum Dr. Anna M. Lackner	Hughes Research, Malibu, CA
June 14	Dr. Werner Becker	E Merck, Darmstadt, Germany
June 14	Dr. Kenji Hayashi Dr. Tetsuo Oka	Toray Industries, Inc., Japan
June 18	Dr. Yukihaza Uemura Dr. Seimei Yasui Dr. Koichi Fjuisama	Sumitomo Chemical Co.
June 20	Dr. Rene Dedroit Dr. J.F. Thomas	Glaverbel, Belgium
June 20	Dr. Dave Laughlin Dr. Vance Holloway	NCR, Dayton, OH
June 24	Dr. P.H.J. Beatty	Cambridge University, United Kingdom
July 25	Barry Speck	BFGoodrich, Hatfield, PA
July 30	Jan Bernkopf	Magnascreen Corp., Pittsburgh, PA
August 6	Bruce Winker	Rockwell Intl., Thousand Oaks, CA
August 20	Sigmund Hagstadt	LXD, Oakwood Village, OH
August 22	George Vestley	3M, St. Paul, MN
August 27	Ron Kasulones	EM, Cleveland, OH

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Professor Ali S. Argon

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

**MECHANICAL PROPERTIES OF STRUCTURAL
POLYMERS**

(Computer Simulation and Key Experiments)

A University Research Initiatives Program

Supported by

Defense Advance Research Projects Agency

Monitored by

Office of Naval Research

under Contract: N00014-86-K-0768

Principal Investigator: Ali S. Argon

Co-Investigators: Robert E. Cohen

David M. Parks

Ulrich W. Suter (ETH-Zurich)

Sidney Yip

January 14, 1992

GENERIC PROBLEMS THAT NEEDED ANSWERS

GLASSY POLYMERS

PLASTIC FLOW	vs.	CRAZING
(Ductile Behavior)		(Premature-Brittle Fracture)
(Inflexible Chain Polymers)		(Flexible Chain Polymers)

PHYSICAL AGING AND EMBRITTLEMENT

SEMI-CRYSTALLINE POLYMERS

DRAWN POLYMERIC FIBER \Rightarrow HIGH MODULUS
CARBON FIBER



TRANSLATES TO LONG RANGE
SCIENTIFIC GOALS

LONG RANGE GOALS

MOLECULAR STRUCTURE OF GLASSY POLYMERS

(Flexible Chain)

(Inflexible Chain)

PP

PC

(Structure of Atomic Glasses)

MECHANISM OF PLASTIC DEFORMATION IN GLASSY POLYMERS

(Incipient Cavitation of Polymers \Rightarrow Crazing

(Mechanism in Atomic Glasses)

(Mechanism in Disordered Solids)

STRUCTURAL RELAXATIONS IN GLASSY POLYMERS

(Melting, Glass Transition)

(In Atomic Glasses)

(in General Disordered Solids)

PLASTIC FLOW IN SEMI-CRYSTALLINE POLYMERS

(Texture Formation and Alteration)

(Spherulitic Morphology \Rightarrow Fiber or Pseudo-Crystal
remains to be modelled)

All are Long Range Fundamental Questions

**All are with Great Potential Rewards for more reliable structural
polymers**

All are amenable to computer simulation

UNIQUE ASPECTS OF PROGRAM

Simulations based on physical molecular or atomic mechanisms

Kinematics and energetics of local structural relaxations in amorphous polymers and atomic glasses are visualized

Mechanics of evolution of deformation textures subject to rigid constraints of chain inextensibility

Once developed, computer codes should handle many boundary value problems for large strain inhomogeneous deformation

Experimental program on morphology and mechanisms is closely tied to simulations of texture and has stimulated the modelling

PROGRAM ORGANIZATION AND STAFFING

TASK I Simulation of Molecular Structure of Glassy Polymers and Plastic Deformation

U.W. Suter, A.S. Argon
Michelle Hutnik (GS)(*)
Peter Mott (GS)(*)
Vasily Bulatov (Visiting Scientist)(*)

TASK II Simulation of Structural Relaxations

S. Yip, A.S. Argon
Mark Sylvester (GS)
Vasily Bulatov (Visiting Scientist)(*)

TASK III Simulation of Texture Forming Deformations in Semi-Crystalline Polymers

D.M. Parks, A.S. Argon
Said Ahzi (PD)(*)
Bing-Jean Lee (PD)

TASK IV Experimental Study of Morphology and Texture Forming Plastic Deformation Mechanisms

R.E. Cohen, A.S. Argon
Zbigniew Bartczak (PD)(*)
Hyun H. Song (PD)(*)
Anuj Bellare (GS)(*)
Julie Anderson (GS, DuPont Fellow)(*)
Li Lin (GS)(PD)
Andrezej Galeski (Visiting Scientist)(*)

(*) Left the program.

SUMMARY OF MAJOR ACCOMPLISHMENTS

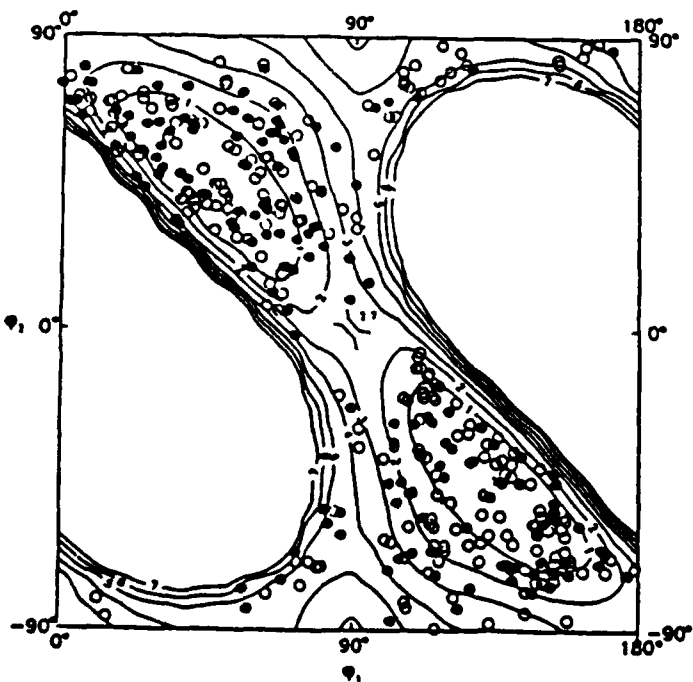
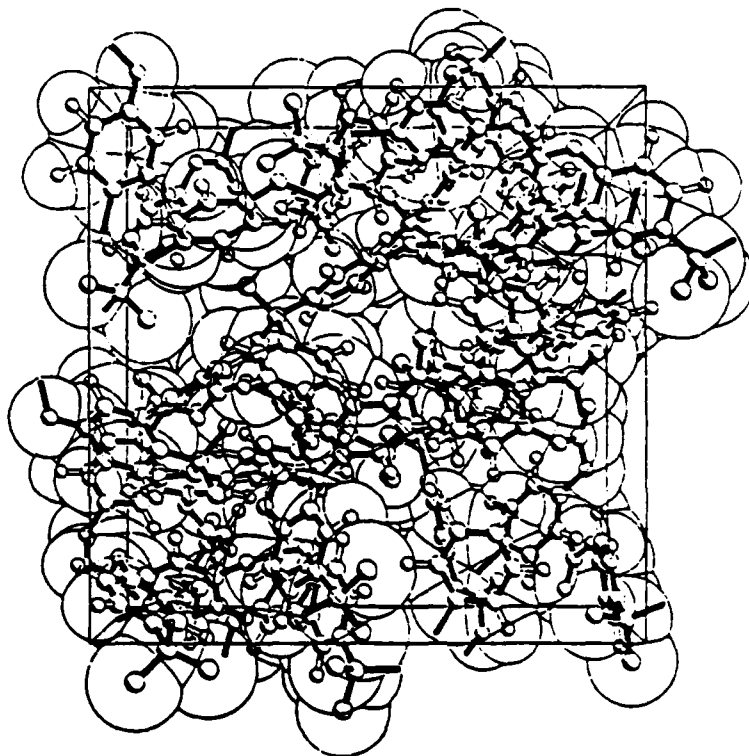
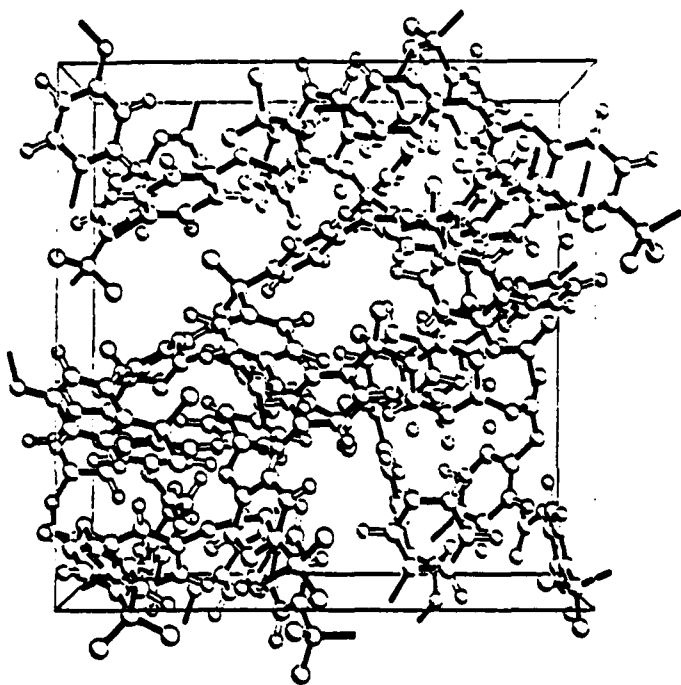
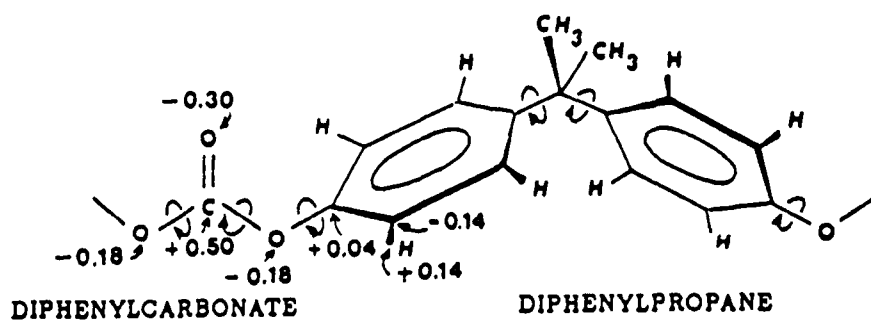
- Extensive study of the dynamic structural properties of model 2-D atomic glasses by molecular dynamics and the modelling of the mechanisms of plastic deformation in it.
- Modelling of structural relaxations, and plastic deformation, their kinematical features and kinetics by a Monte Carlo technique based on Eshelby transformations.
- Simulation of the structure of PC, its energetics; and the kinematics of ring flips, and carbonate group rotations.
- Small strain elastic properties and large strain plastic deformation of glassy PC.
- Simulation of plastic flow and its kinematics in polypropylene elucidating the very cooperative nature of unit plastic events.
- Simulation of inelastic dilatation of polypropylene as a precursor for craze initiation.
- Fully flexible molecular dynamics model simulating structural relaxations under constant pressure and temperature in polypropylene.
- Topological features of a glass transition in polypropylene, leading to a radically new interpretation.
- Development of a new formalism of micromechanics of constrained deformation of large assemblies of lamellar polycrystals. prediction of realistic deformation textures in PE, and Nylon 6. New formalism has wide applicability to also hexagonal and other crystals with constrained deformation.
- Development of means of highly oriented semi-crystalline polymers (Nylon, PE, PET) in bulk. Determination of the yield surfaces of highly textures (quasi single crystal) Nylon and PE for use in computer codes. New insight into long period of PE.
- Elastic properties of highly textured Nylon.
- Morphological alteration in plane strain, compression, uniaxial compression, and simple shear in PE and Nylon leading to texture evolution.
- Plastic deformation and early texture evolution in isotactic PS.
- Dislocation mechanisms of plastic shear in quasi-crystalline highly oriented PE.

OVERVIEW OF ACCOMPLISHMENTS IN TASK I

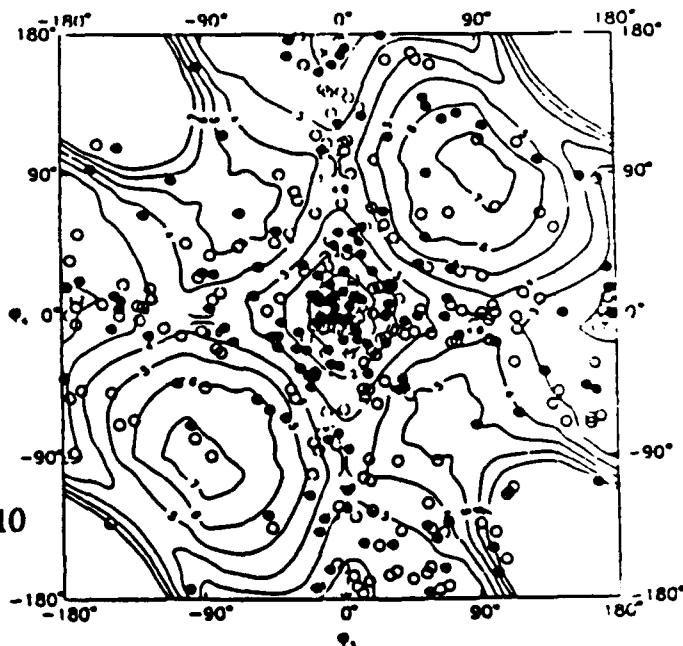
(Suter, Argon, Bulatov, Deng, Hutnik, Mott)

- o Structure of glassy polycarbonate (PC), elastic and an-elastic properties: ring rotations, carbonate group relaxations, and their energetics.
- o Large strain plastic deformation in glassy polypropylene and polycarbonate: similarities and differences between these flexible and stiff chain polymers
- o Cavitation response of polypropylene to negative pressure: precursor to crazing
- o Plastic deformation in 2-D atomic glass models
- o Plastic deformation in 2-D models of generic amorphous elastic media

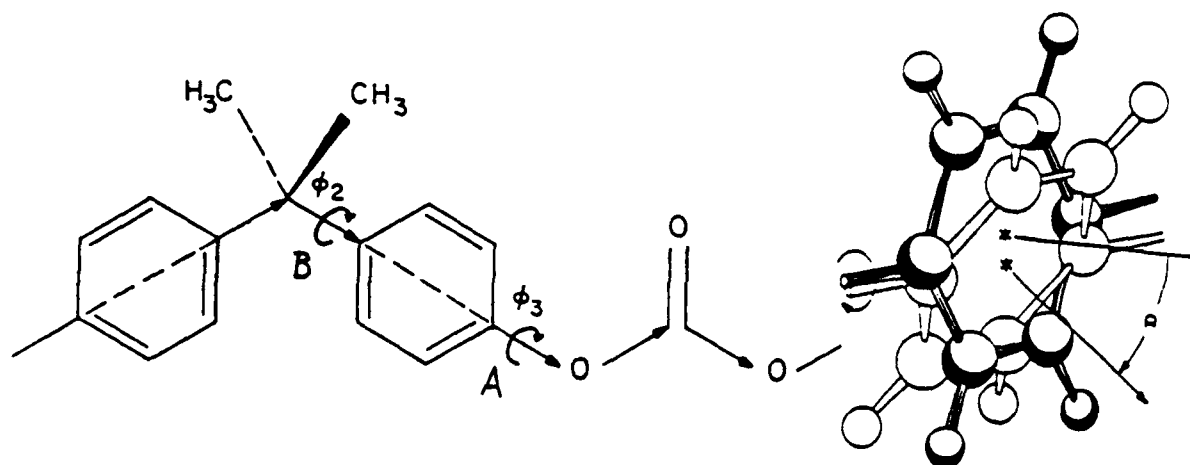
POLYCARBONATE OF BISPHENOL-A



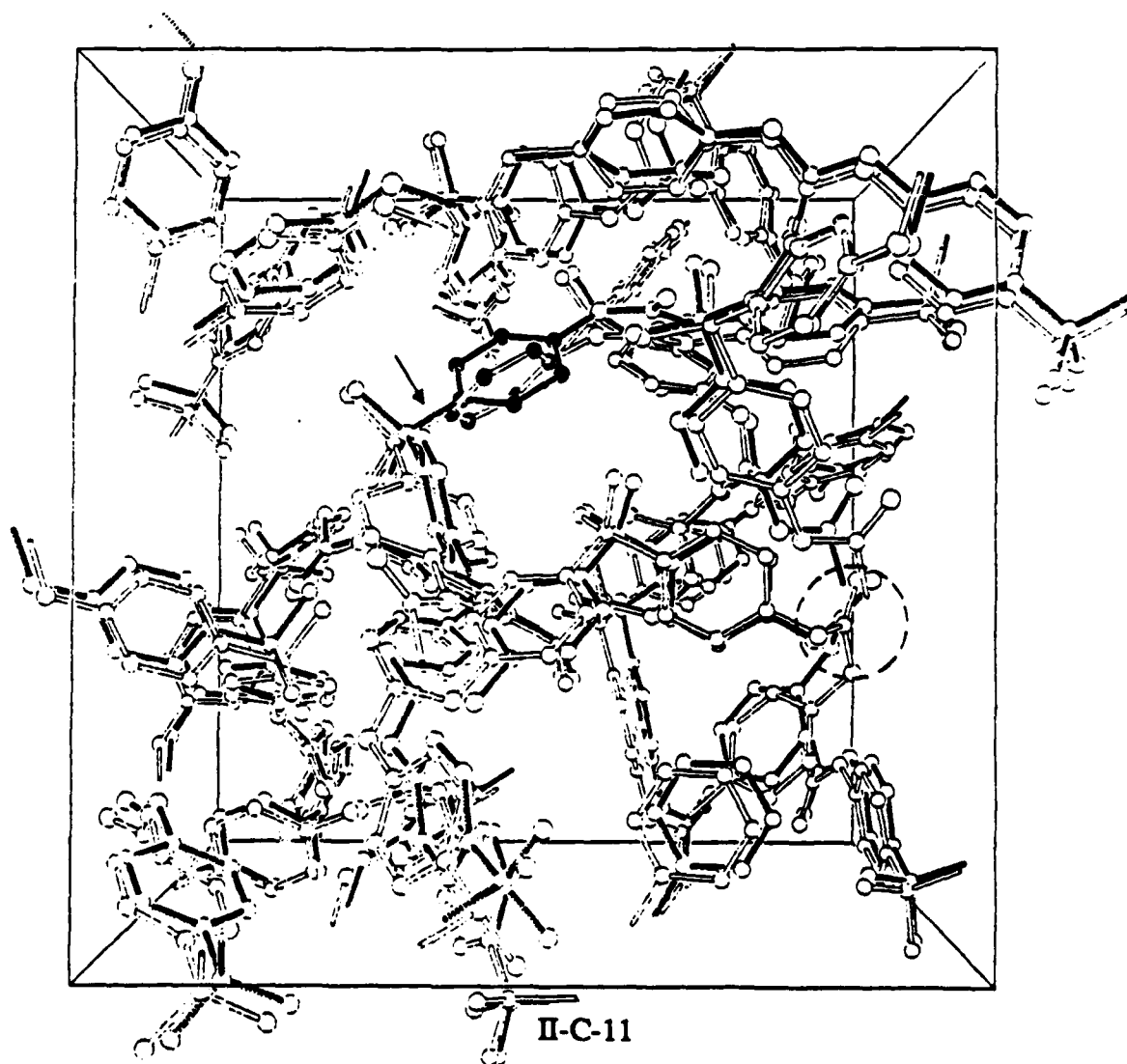
II-C-10



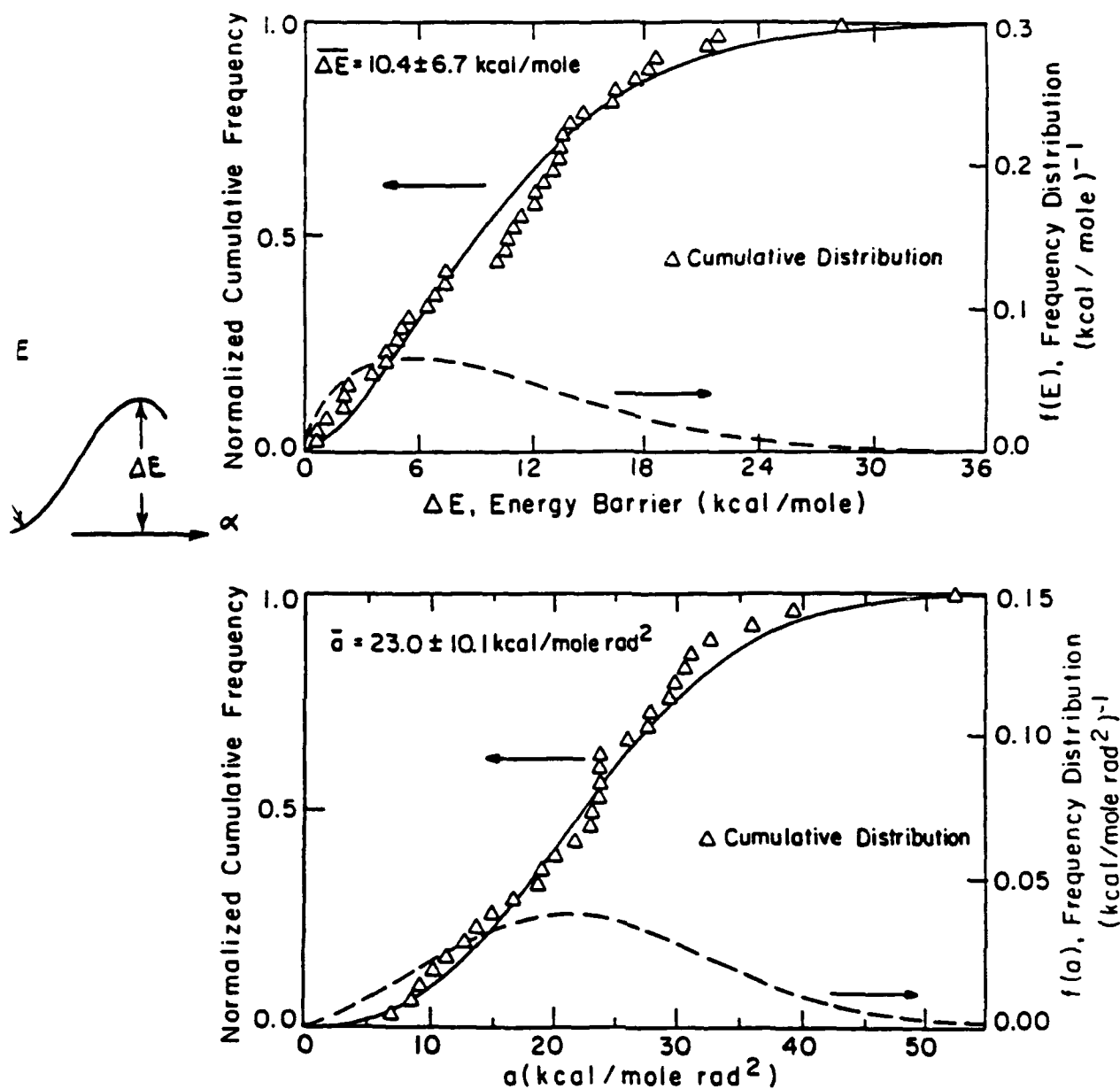
ANELASTIC RESPONSE IN BPA-PC
(ENERGETICS OF PHENYLENE RING ROTATIONS)



MOLECULAR MOTIONS ASSOCIATED WITH RING
ROTATIONS



TYPE A: RING ROTATION RESPONSE Energy Barrier Spectrum



• Experimental values for barrier to ring motion:

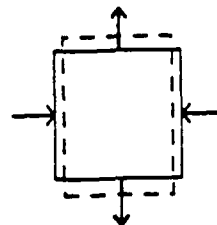
- ¹H NMR (Jones et al., 1983): 12 Kcal/mole
- ¹³C NMR (Schaefer et al., 1984): 11 Kcal/mole
- ¹³C NMR (Roy et al., 1986): 12 Kcal/mole
- ²H NMR (Schmidt et al., 1985): 9.1 Kcal/mole

PLASTIC SHEAR SIMULATION IN GLASSY POLYPROPYLENE

Strain steps imposed on periodic box:

y Axial Extension: $\begin{bmatrix} -1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & -1 \end{bmatrix} \times 10^{-3}$

xy Pure Shear: $\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \times 10^{-3}$



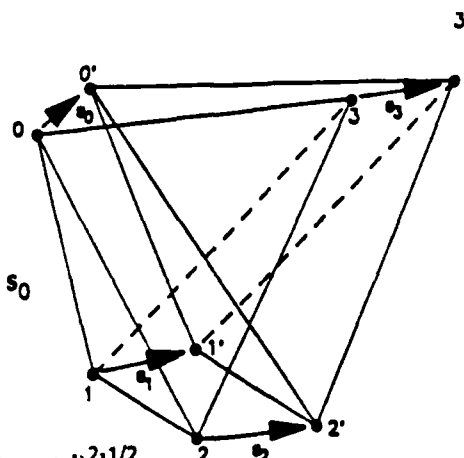
Impose strain increment,
then re-minimized energy, 100 steps.

Atomic level strain

$$\epsilon = \frac{1}{2} \left[\frac{\partial u}{\partial x} + \frac{\partial u}{\partial x} \right], \text{ where } u = s - s_0$$

Invariants Dilatation: $\epsilon = \frac{1}{3} \text{Tr}(\epsilon)$

Work eq. shear: $\gamma = \frac{3}{2} \text{Tr}[(\epsilon - \epsilon I)^2]^{1/2}$

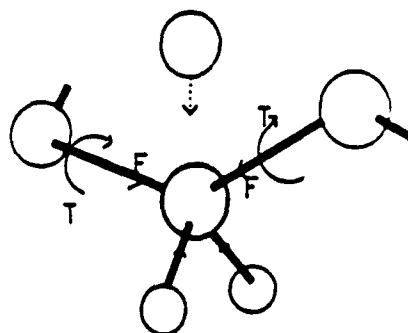


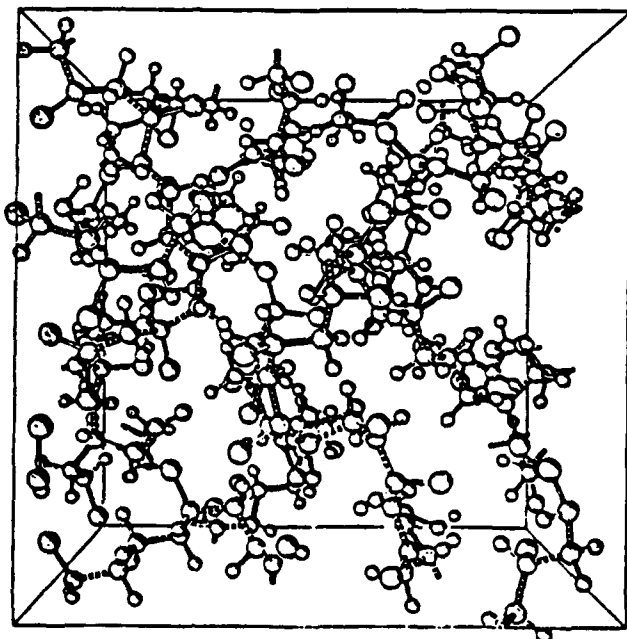
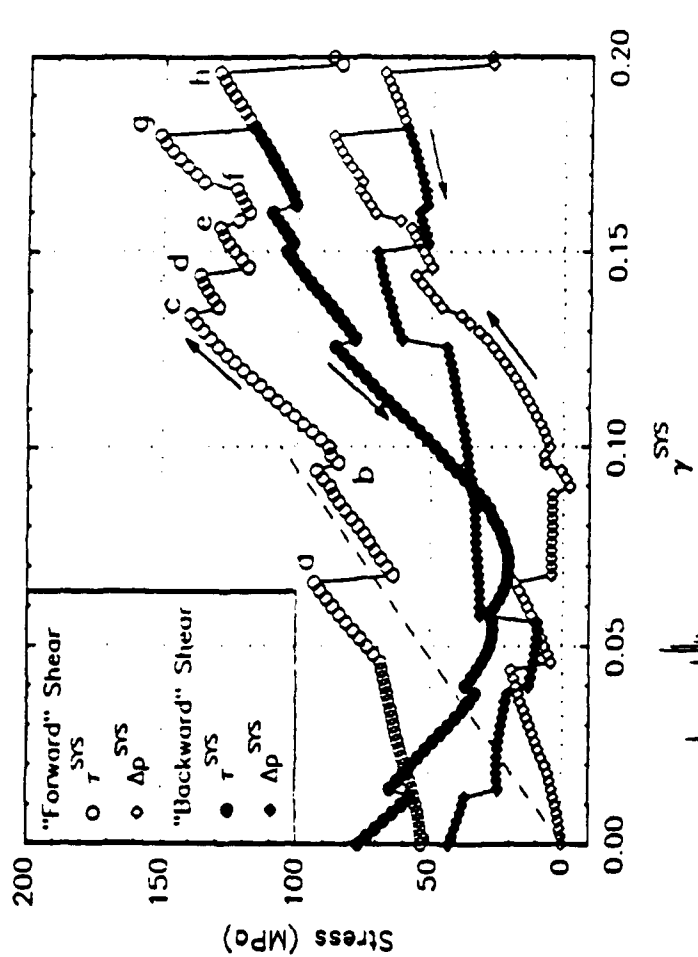
Atomic level stress

$$\sigma_i = - \frac{1}{2V_i} \sum_{j \neq i} \left[r_{ij} F_{ij} + e \frac{T_{ij}}{2} \right]$$

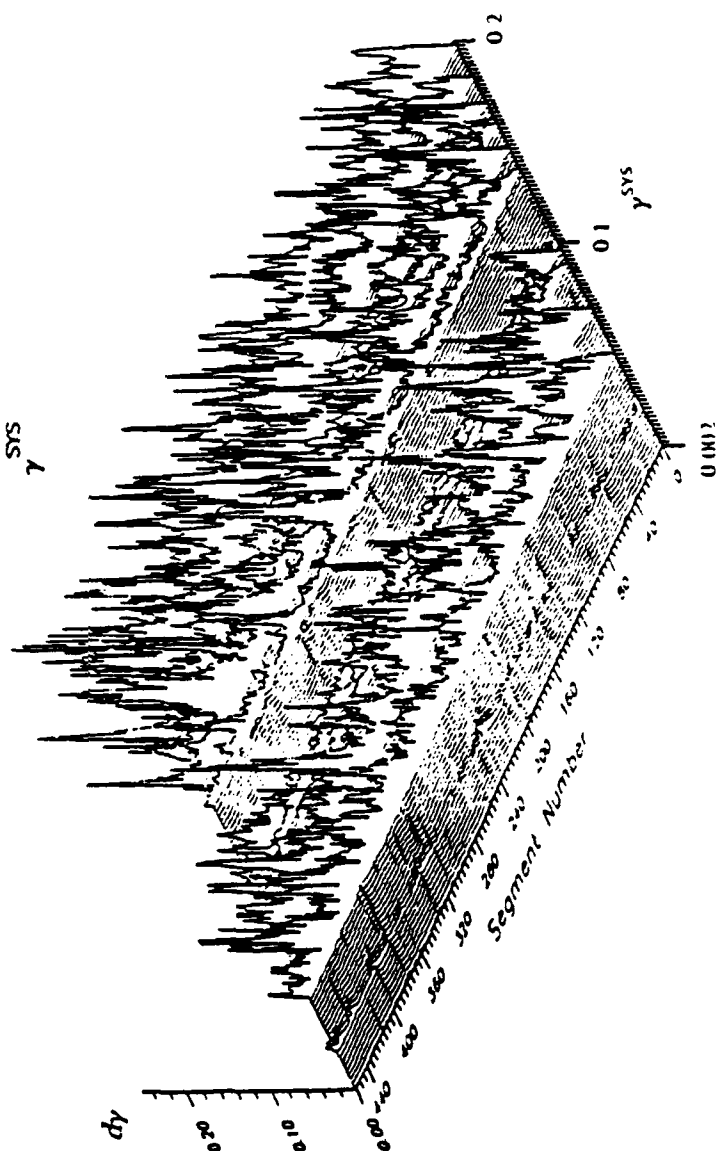
Invariants Pressure: $P = - \frac{1}{3} \text{Tr}(\sigma)$

Von Mises shear: $\tau = \frac{1}{2} \text{Tr}[(\sigma - \sigma I)^2]^{1/2}$

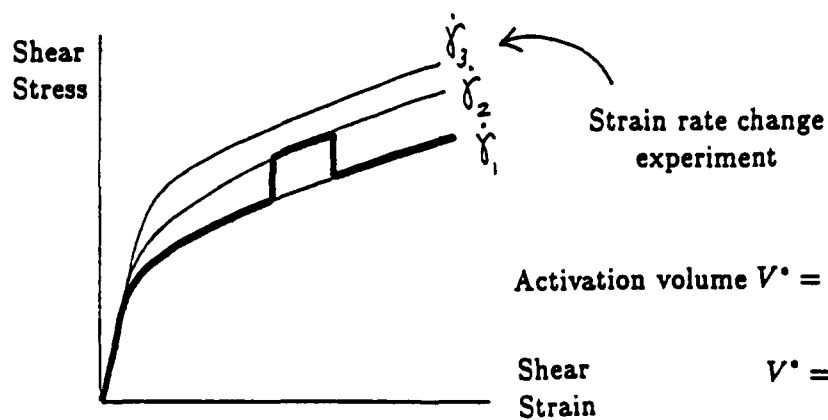
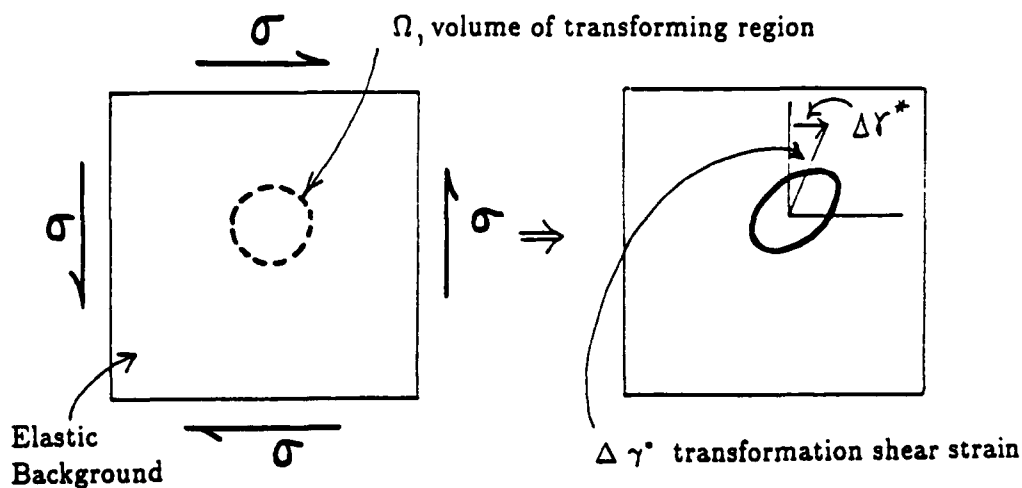




II-C-14

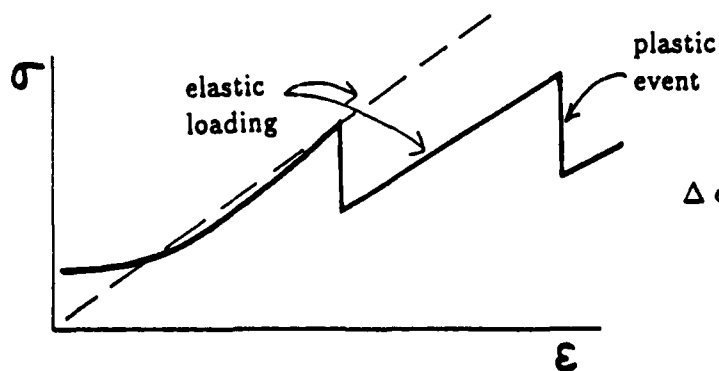


TRANSFORMATION STRAIN INCREMENTS FROM PLASTIC STRESS DROPS



$$\text{Activation volume } V^* = -\frac{\delta \Delta G^*}{\delta \sigma} = \Omega \Delta \gamma^*$$

$$V^* = kT \frac{\delta \ln \dot{\gamma}}{\delta \sigma}$$

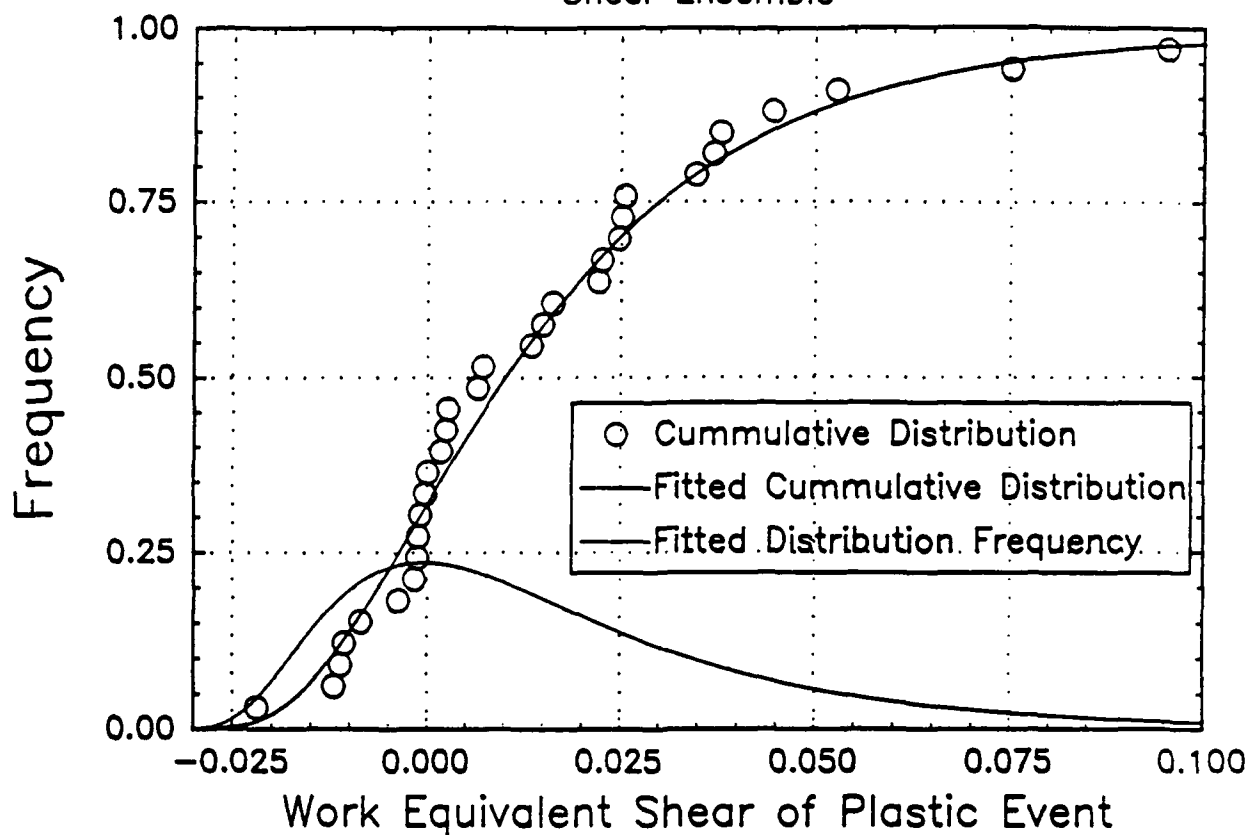


$$\Delta \epsilon_p^* = -\Delta \epsilon_e = -\frac{\Delta \sigma}{E}$$

$$\Delta \gamma^* = \sqrt{3} \Delta \epsilon_p^*$$

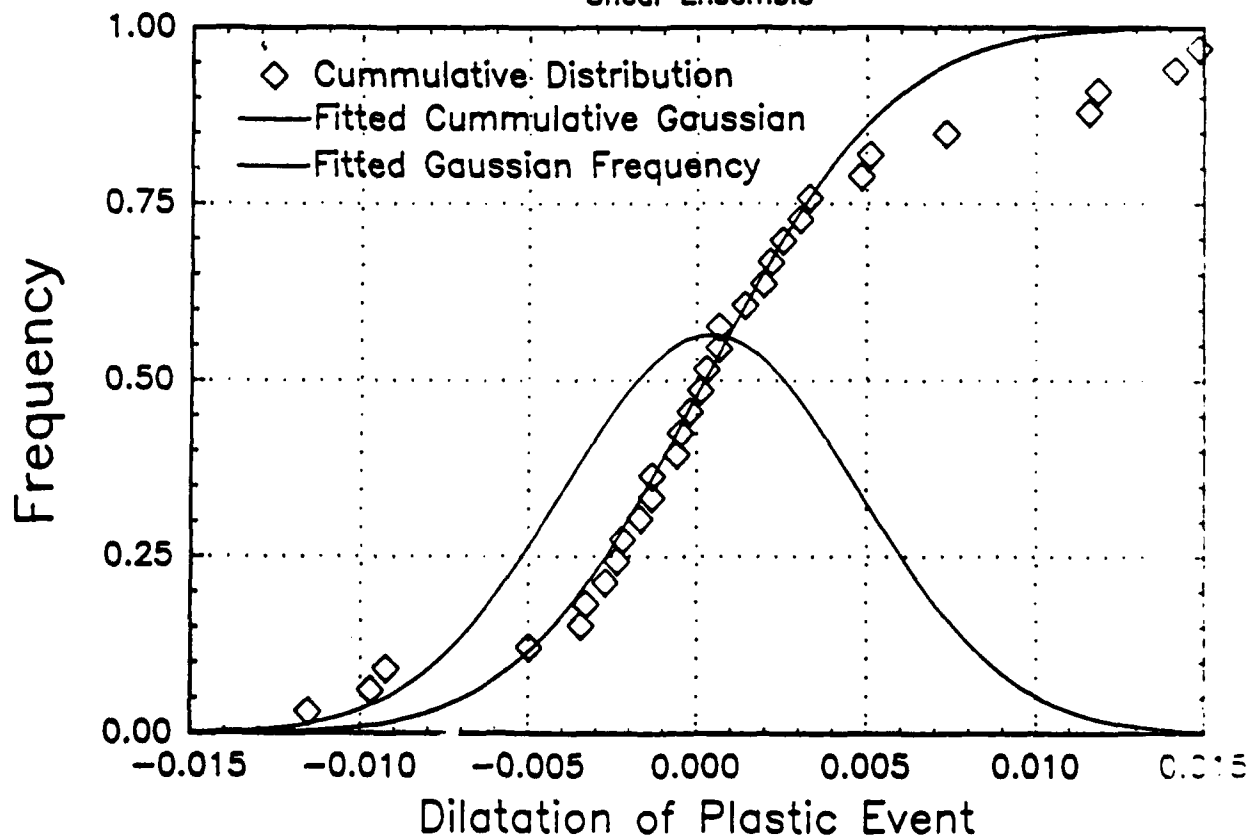
Distribution of Plastic Strain

Shear Ensemble



Distribution of Dilatation

Shear Ensemble



SIMULATION RESULTS COMPARED WITH EXPERIMENTS

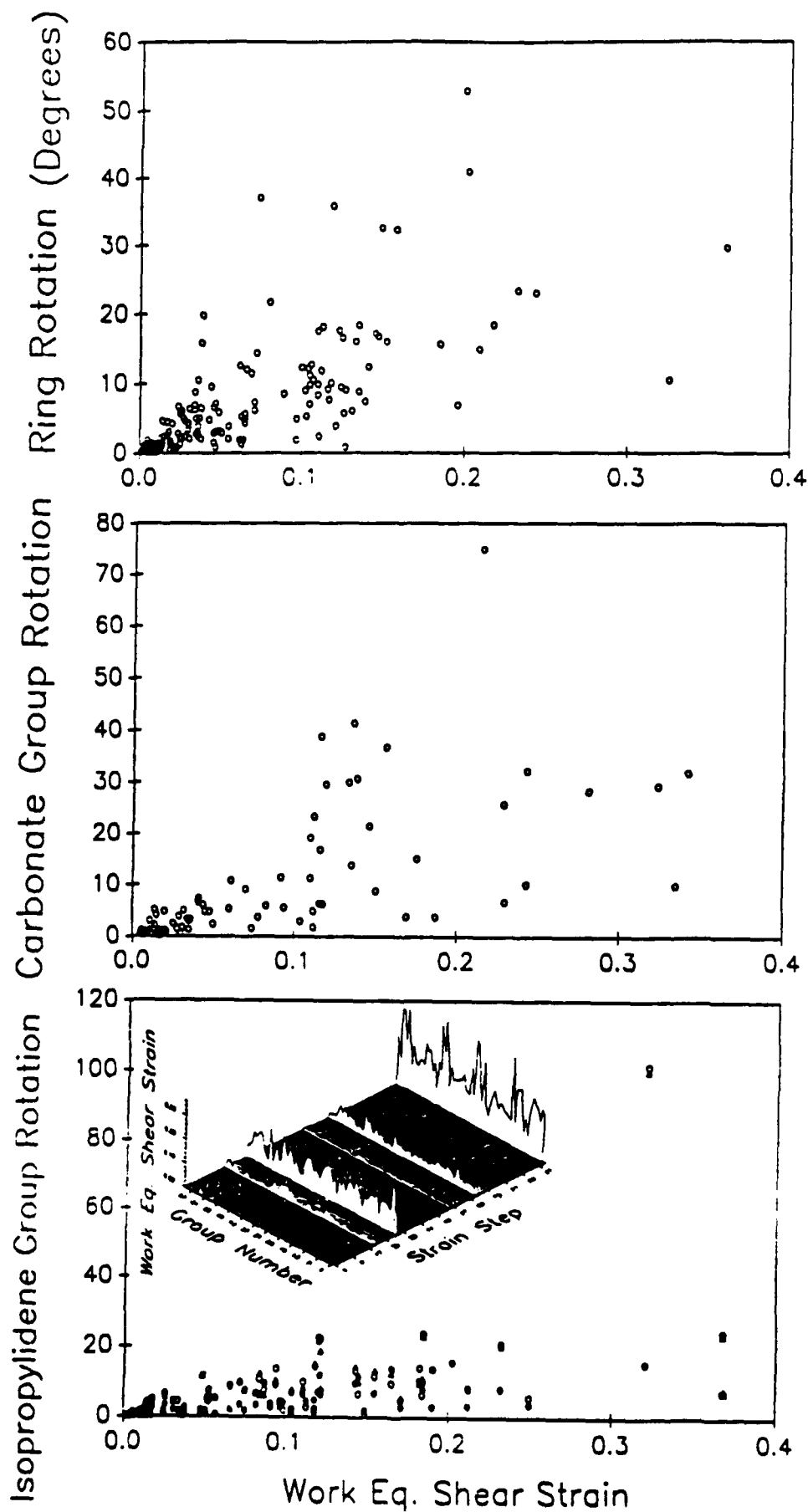
TRANSFORMATION SHEAR STRAIN FROM SIMULATION OF PLASTIC FLOW IN POLYPROPYLENE

$$\bar{\Delta}\gamma^* = 0.037, \quad \sigma(\bar{\Delta}\gamma^*) = 0.035$$

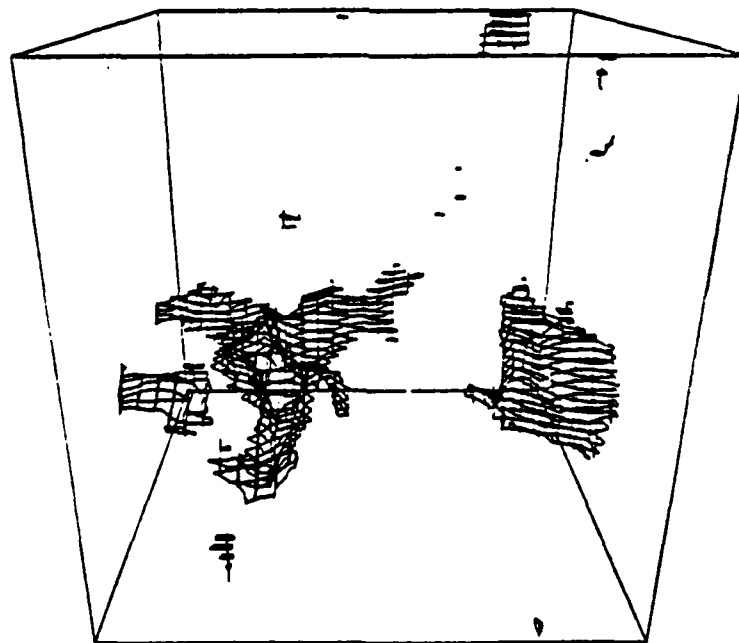
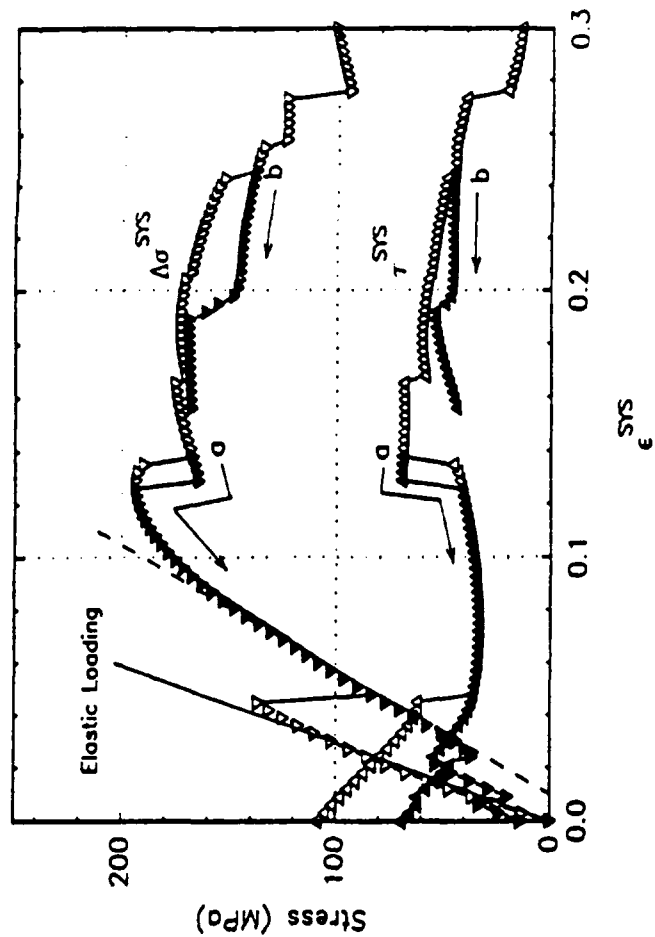
EXPERIMENTALLY MEASURED ACTIVATION VOLUMES IN STRAIN RATE CHANGE EXPERIMENTS (Argon and Bessonov, 1977)

$$\Delta v^* = \Omega \Delta \gamma^* = - \left(\frac{\partial \Delta G^*}{\partial \sigma} \right)_{p,T} = kT \left(\frac{\partial \ln \dot{\gamma}}{\partial \sigma} \right)_{p,T}$$

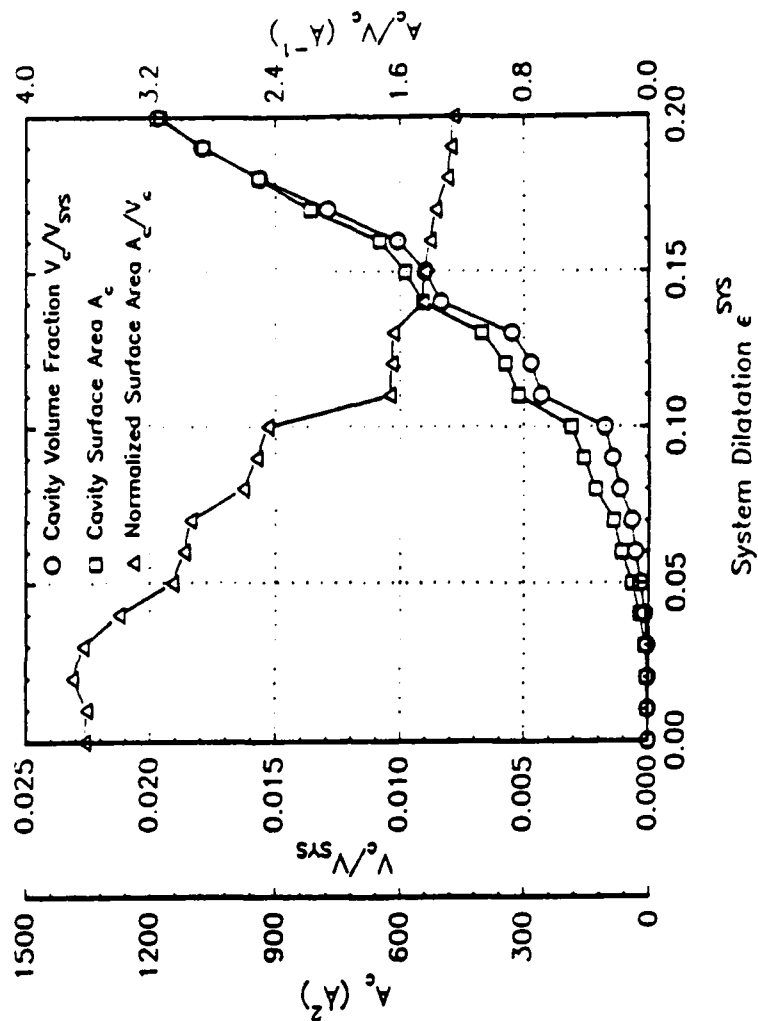
	PS	PMMA	PPO	PET	PC	Kapton
$\Delta v^*, (\text{\AA}^3)$	1142	1510	2464	3985	4262	9157
$\Omega, (\text{\AA}^3)$	3.09×10^4	4.08×10^4	6.66×10^4	1.08×10^5	1.15×10^5	2.47×10^5
$d, (\text{\AA})$	38.9	42.7	50.3	59.1	60.3	77.9
$\Delta v^* = kT(\partial \ln \dot{\gamma} / \partial \sigma); \Omega = \Delta v^* / \Delta \gamma^*; d = (6\Omega/\pi)^{1/3}$						



DILATATIONAL RESPONSE OF POLYPROPYLENE



WISPY SHAPES OF CAVITIES



CONCLUSIONS

Plastic flow in a glassy polymer is by shear transformations having a typical magnitude of c.a. $\Delta\gamma^T = 0.04$ occurring in volume elements of c.a. 5-6 nm dimensions.

Shear transformations most often are dilatant.

Molecular motions are complex and relaxations occur primarily by torsional bond rotations.

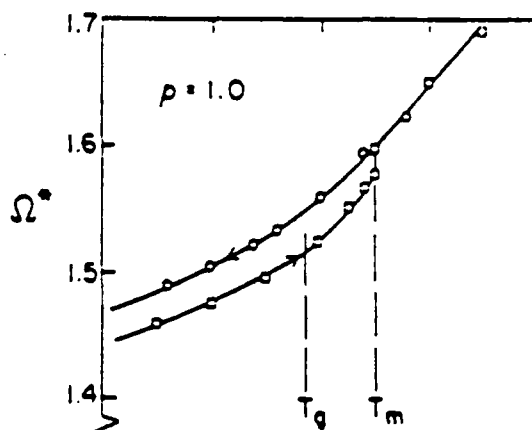
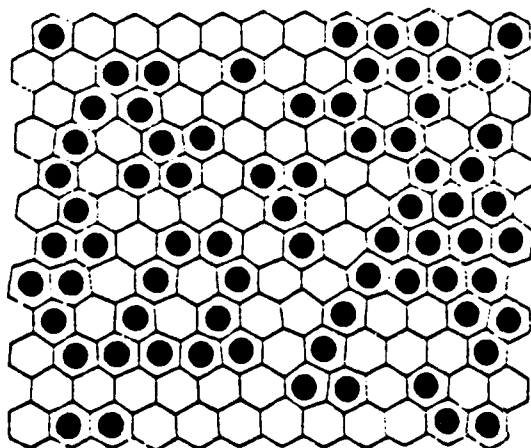
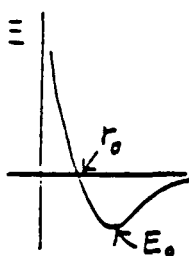
In complex molecules with "rigid" groups (phenyl rings, carbonate groups in PC) rotational relaxations of such groups contribute importantly to the transformation strain. They play an important role in anelastic response.

In early phases of deformation molecular alignment is very weak and almost negligible.

MELTING, GLASS TRANSITION AND STRUCTURAL RELAXATIONS (AGING) IN A 2-D ATOMIC GLASS (Molecular Dynamics Under Constant Pressure)

Deng (Argon, Yip)

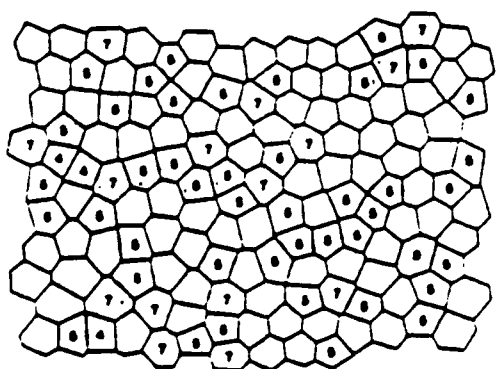
(periodic BC)



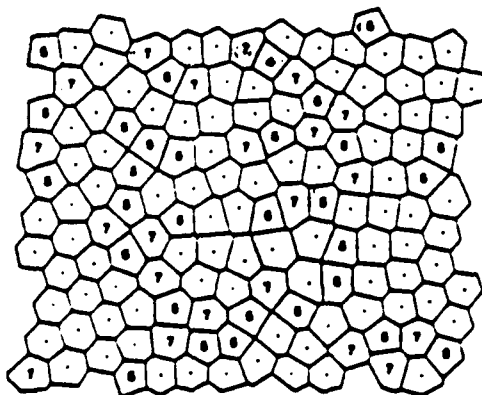
$$T_m = 0.25(E_0/K)$$

$$T_g = 0.18(E_0/K)$$

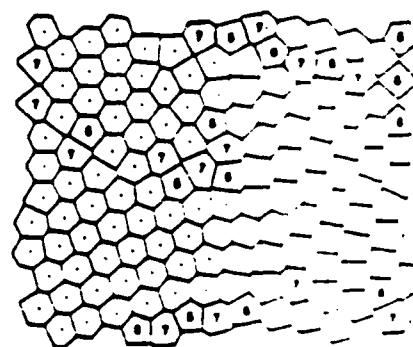
$T > T_m$



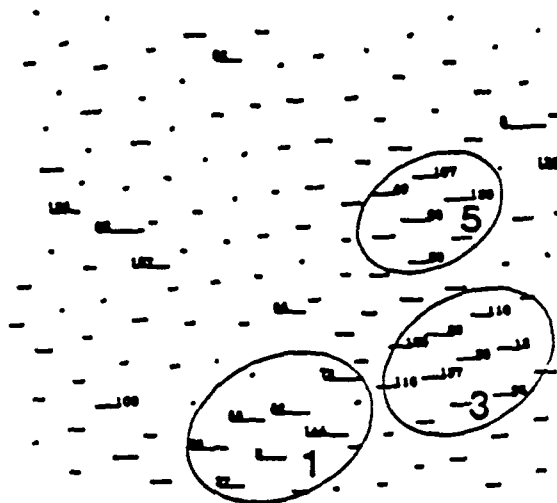
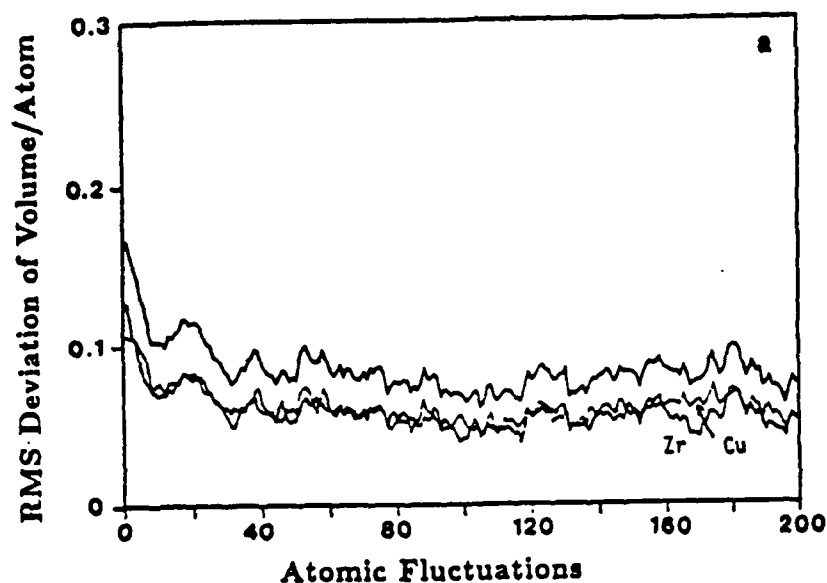
$T_m > T > T_g$



$T < T_g$

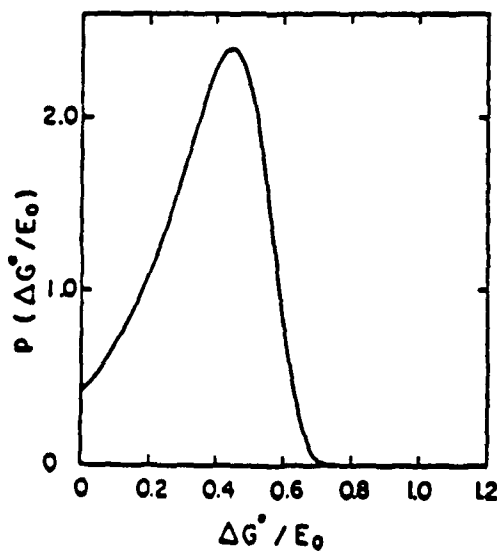


KINETICS OF STRUCTURAL RELAXATIONS (AGING) IN A 2-D ATOMIC GLASS



$$\psi(t) = \exp \left(\frac{-t}{\tau_w} \right)^\beta$$

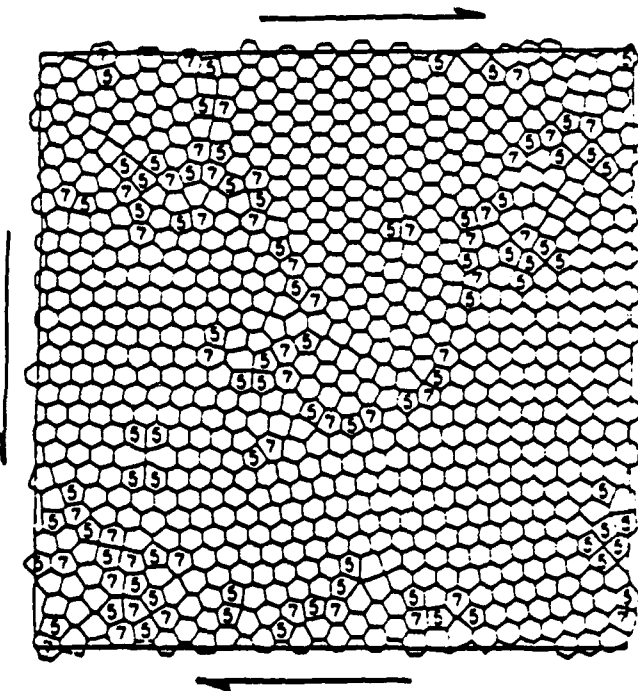
Kinetics follows Williams and Watts. Equation with
exponent of 0.5



SIMULATION OF PLASTIC DEFORMATION IN A TWO DIMENSIONAL ATOMIC GLASS BY MOLECULAR DYNAMICS

$$\Delta \gamma = 5 \times 10^{-4}$$

$$T/T_m = 4 \times 10^{-3}$$



$$\sigma_{\alpha\beta}(i) = \frac{1}{2\Omega_i} \sum_{j \neq i} \left[\frac{\partial \Phi(r)}{\partial r} \right]_{r=r_{ij}} \frac{r_{ij}^\alpha r_{ij}^\beta}{r_{ij}}$$

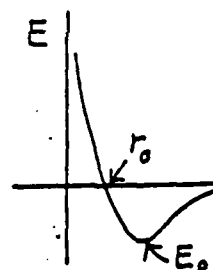
$$r_i = \sqrt{(\sigma_{xy}(i))^2 + \left(\frac{\sigma_{xx}(i) - \sigma_{yy}(i)}{2} \right)^2}$$

$$p_i = -\frac{1}{2} (\sigma_{xx}(i) + \sigma_{yy}(i))$$

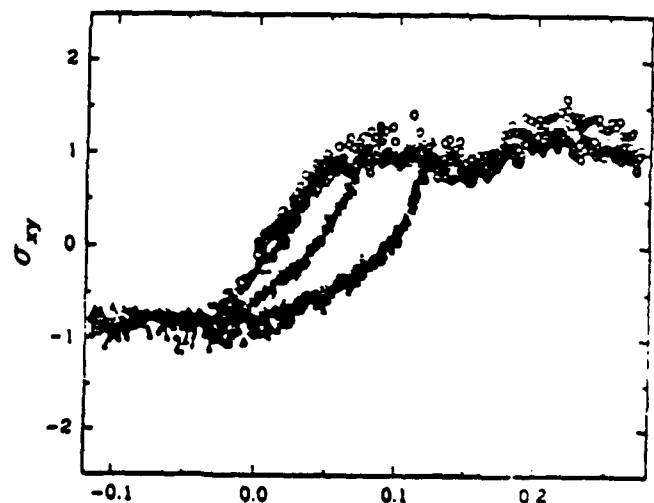
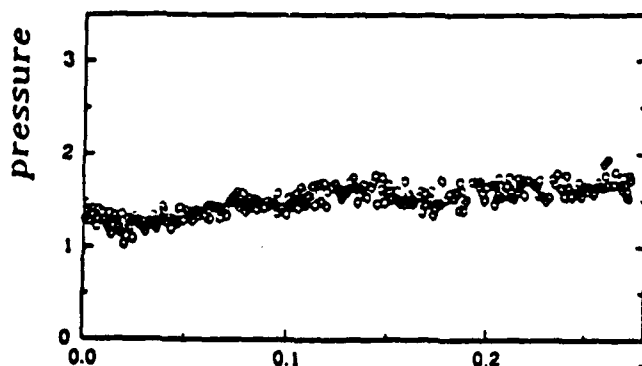
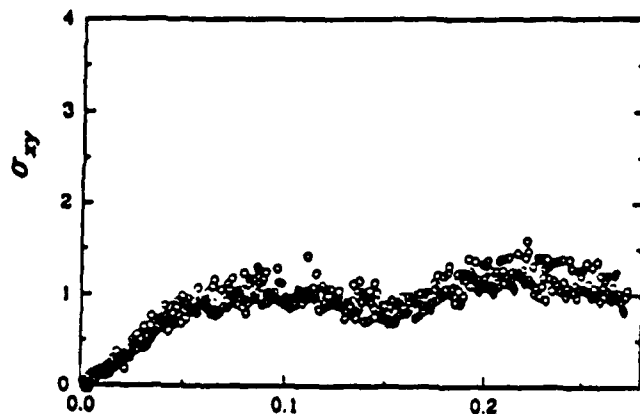
$$\Delta \epsilon_{\alpha\beta}(i, \Delta t) = \frac{1}{2s_i} \int_{s_i} \left(\frac{\partial \Delta u_\alpha}{\partial \beta} + \frac{\partial \Delta u_\beta}{\partial \alpha} \right) ds$$

$$\Delta \gamma_{mas}(i) = 2\sqrt{(\Delta \epsilon_{xx}(i) - \Delta \epsilon_{yy}(i))^2 + (\Delta \epsilon_{xy}(i))^2}$$

$$\Delta \epsilon(i) = \Delta \epsilon_{xx}(i) + \Delta \epsilon_{yy}(i)$$



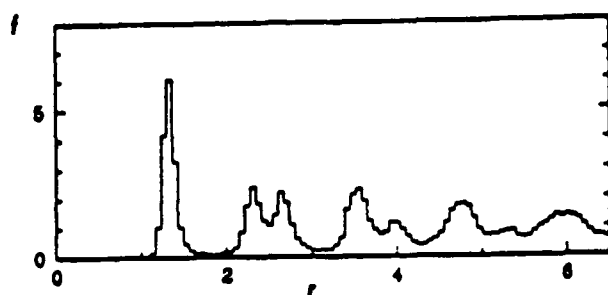
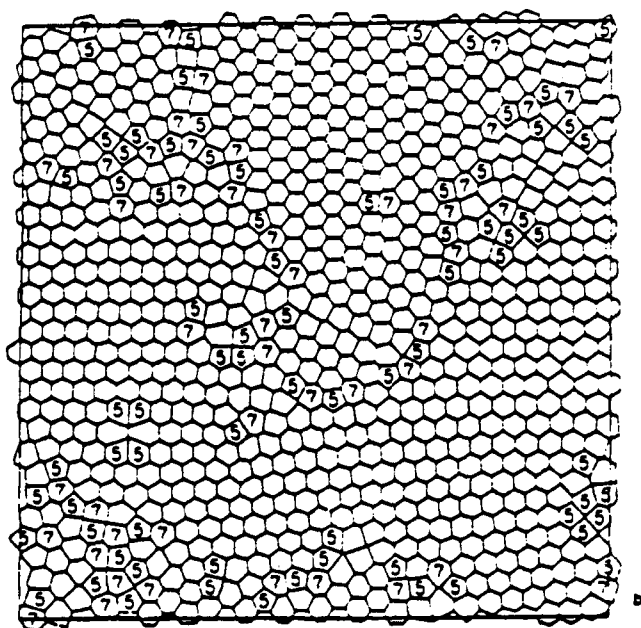
Unit of stress E_0/r_0^2



II-C-23

γ

γ

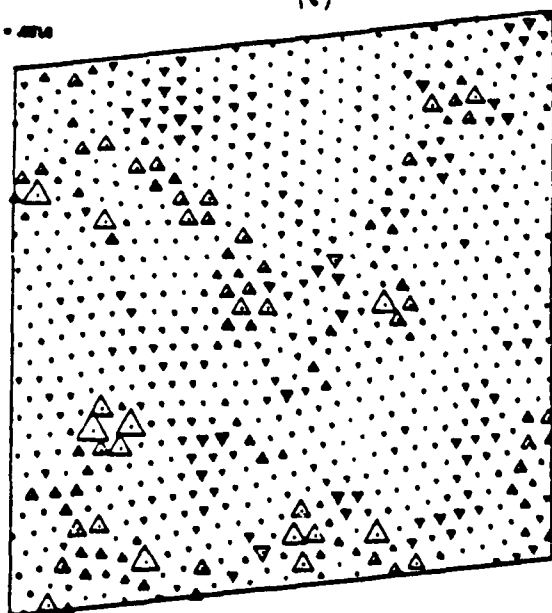


$\Delta = .2$

FREE VOLUME

(c)

7-0010

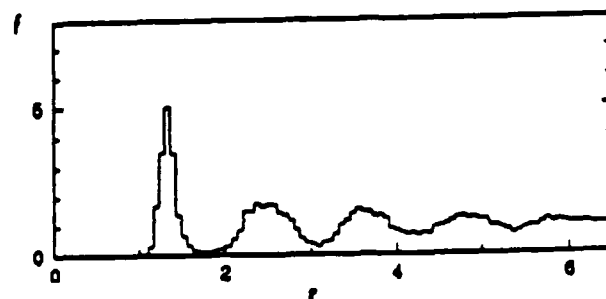
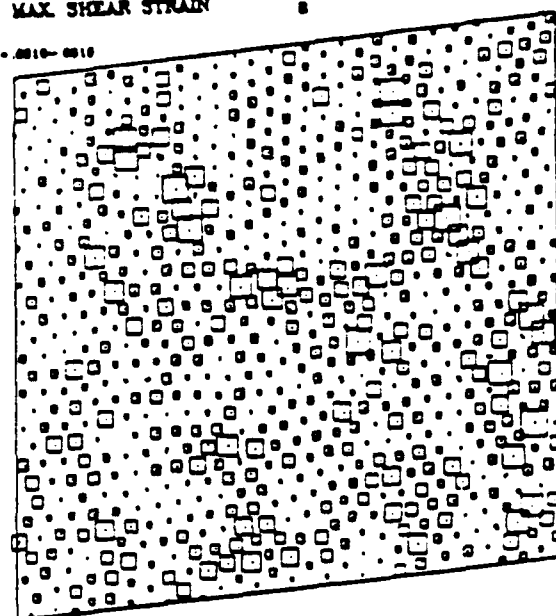


$\square = .10$

MAX. SHEAR STRAIN

8

47-0010-0010

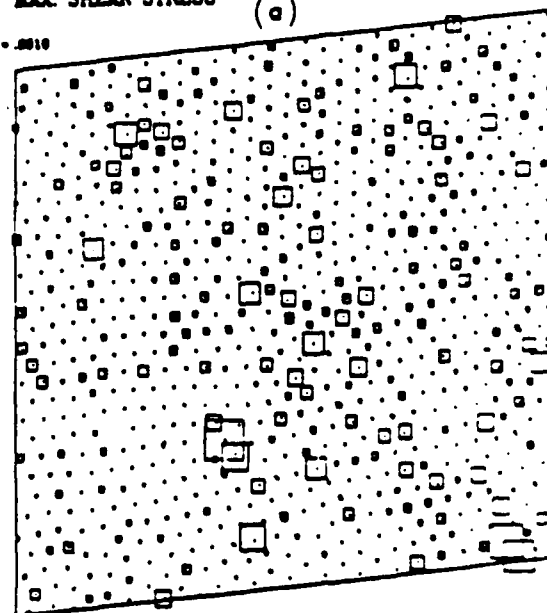


$\square = 5.0$

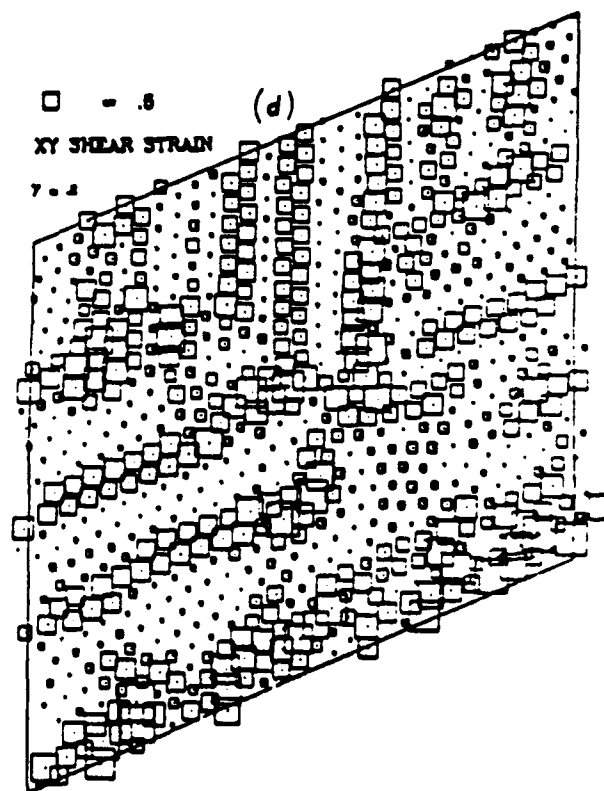
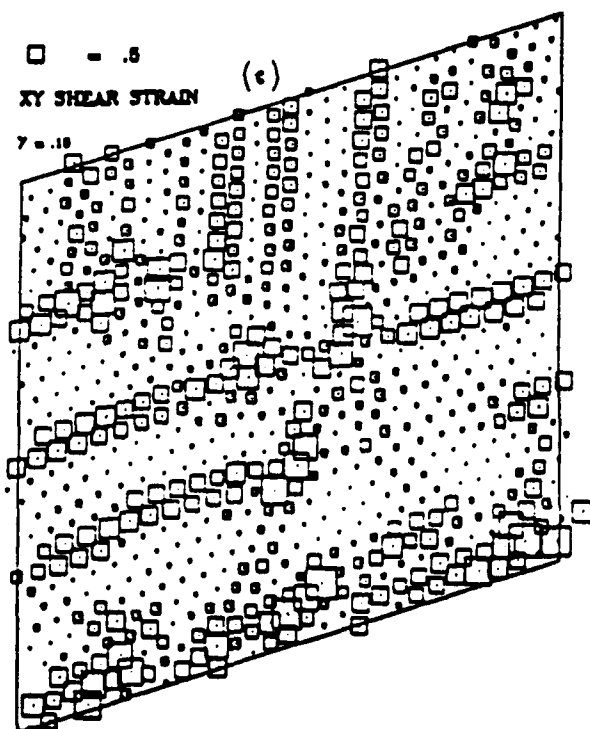
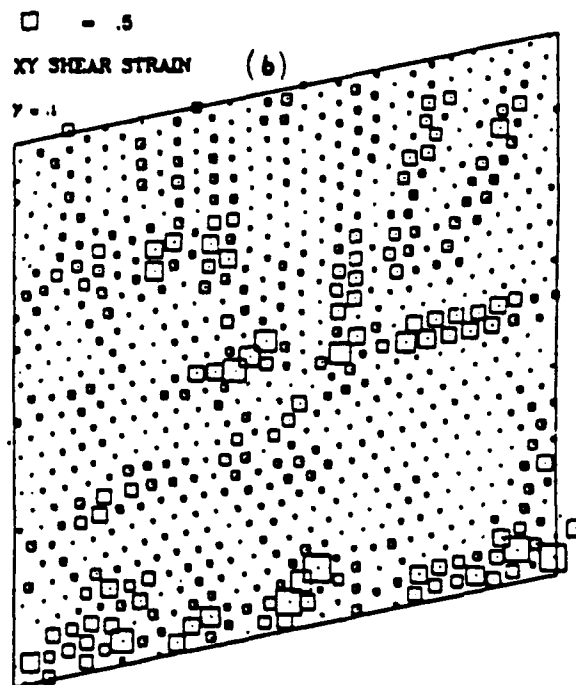
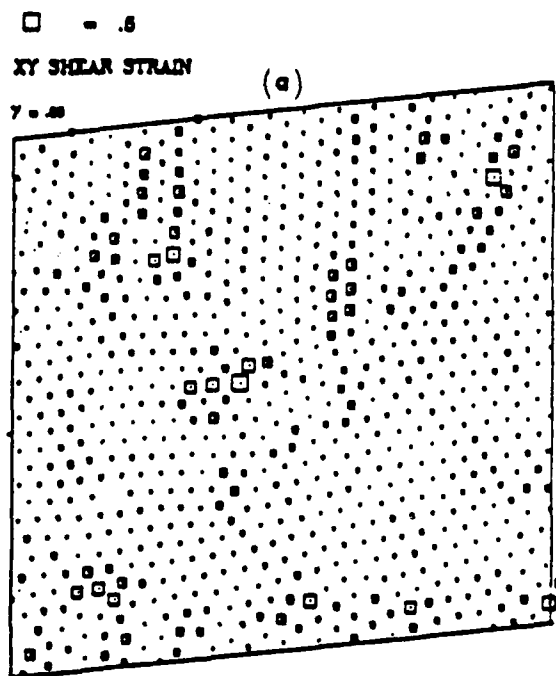
MAX. SHEAR STRESS

(a)

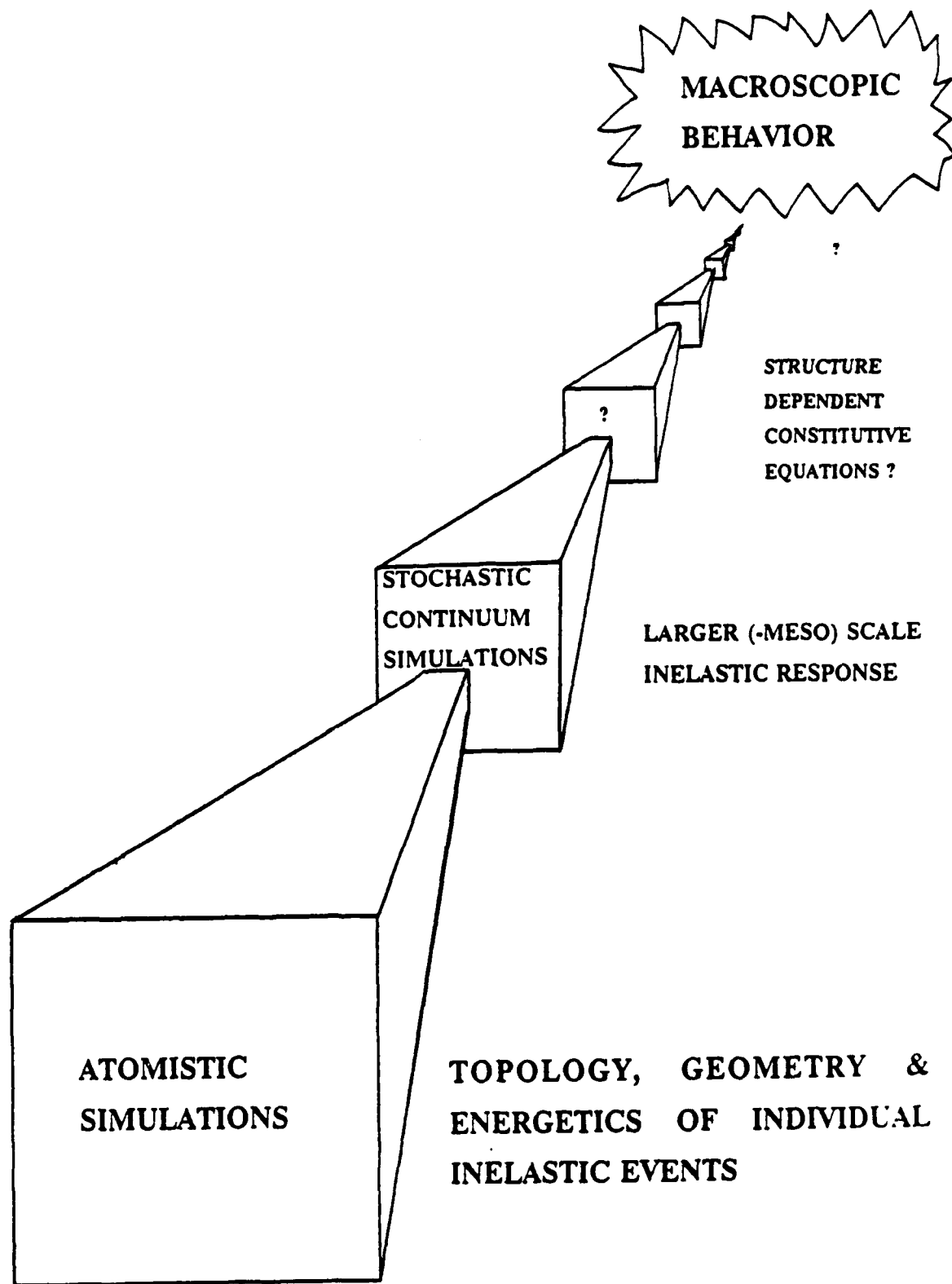
7-0010



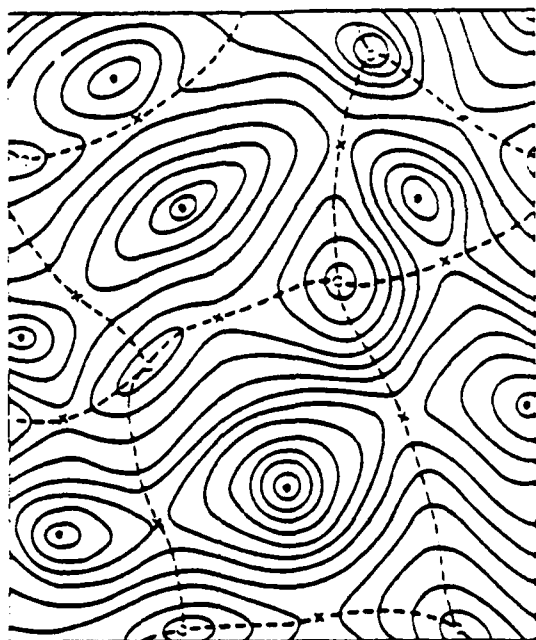
SHEAR LOCALIZATION DUE TO DILATANCY OF DEFORMATION



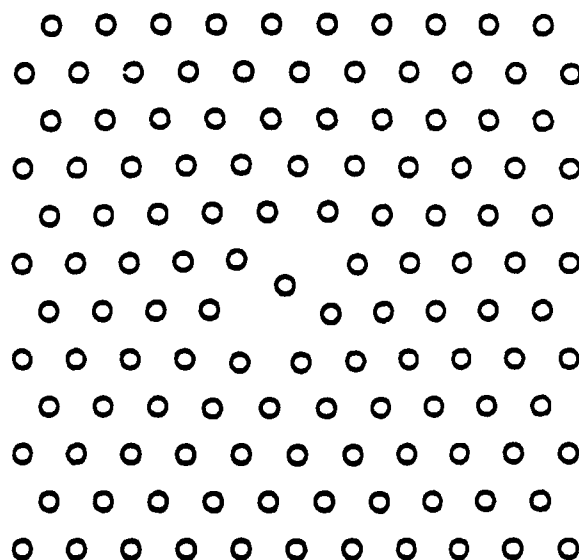
SUMMARY: Percolation of liquid-like material through structure at melting.
Percolation broken below T_g .
Structural relaxations in clusters.
Kinetics requires time scaling.
Plastic flow by local shear transformations in frozen-in liquid-like material.
Shear localization by dilatancy.



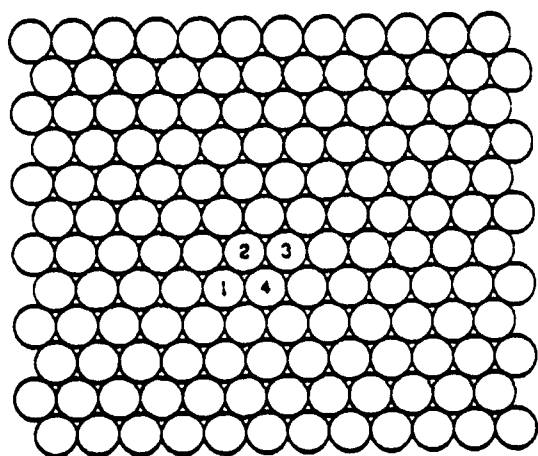
How to identify and characterize local inelastic transformations?



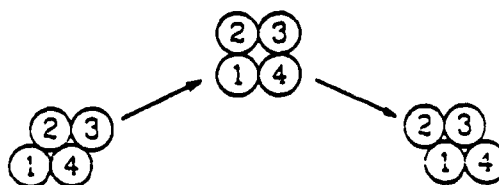
Schematic representation of the potential-energy hypersurface. Open circles are maxima, solid circles are minima. Saddle points are indicated by crosses. The solid curves are equipotential loci. Dotted curves passing through saddle points and converging at maxima represent boundaries of the steepest-descent basins that surround each local minimum.



A simple saddle-point configuration

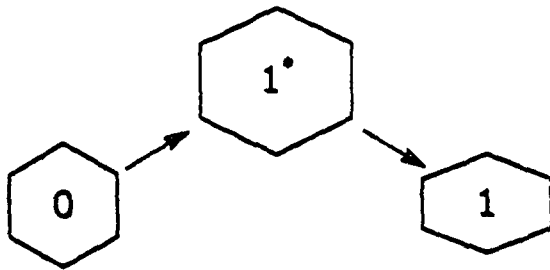


A fragment of the hexagonal packing

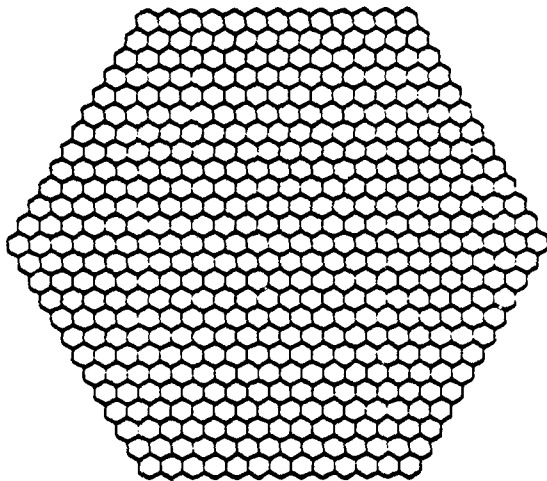


A simple shear transformation of four-particle cluster
II-C-28

An idealized 2-D elasto-plastic continuum

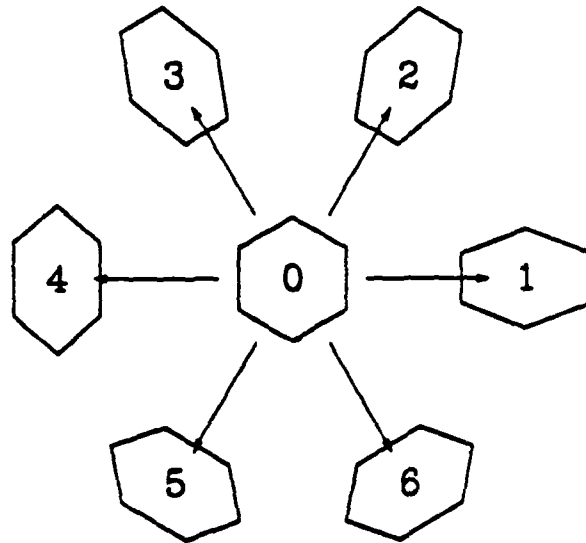


A shear transformation of the hexagon



A fragment of the hexagonal tessellation

The complete set of 6 inelastic transformations allowed



The model:

1. Plastic flow is treated as a net result of *local inelastic shear transformations (LISTs)* with transition rates calculated according to the transition rate theory as

$$\omega = \omega_0 \exp \left\{ -\frac{\Delta G(\sigma^{local})}{kT} \right\} ,$$

where

$$\Delta G(\sigma^{local}) = \Delta F_0 - \Omega \sigma_{ij}^{local} \cdot \Delta e_{ij}^*$$

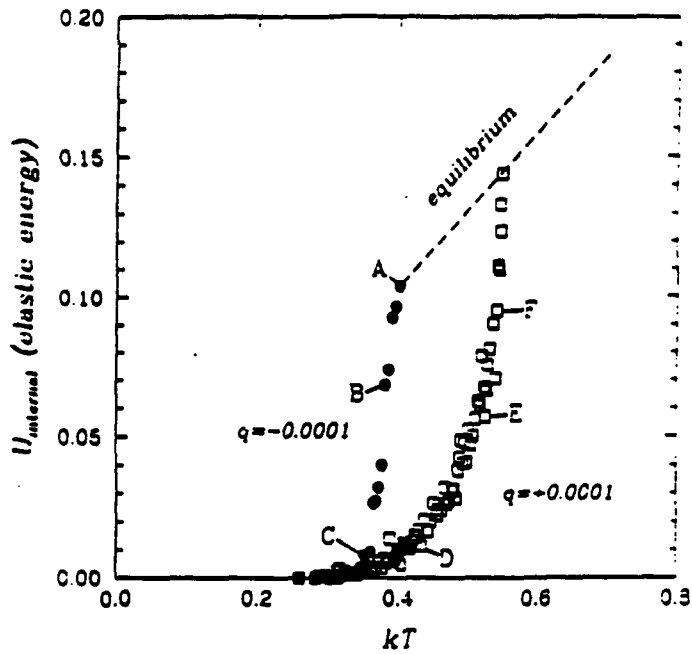
and

$$\sigma_{ij}^{local} = \sigma_{ij}^{external} + \sigma_{ij}^{internal} , \quad \langle \sigma_{ij}^{local} \rangle_V = \sigma_{ij}^{external}$$

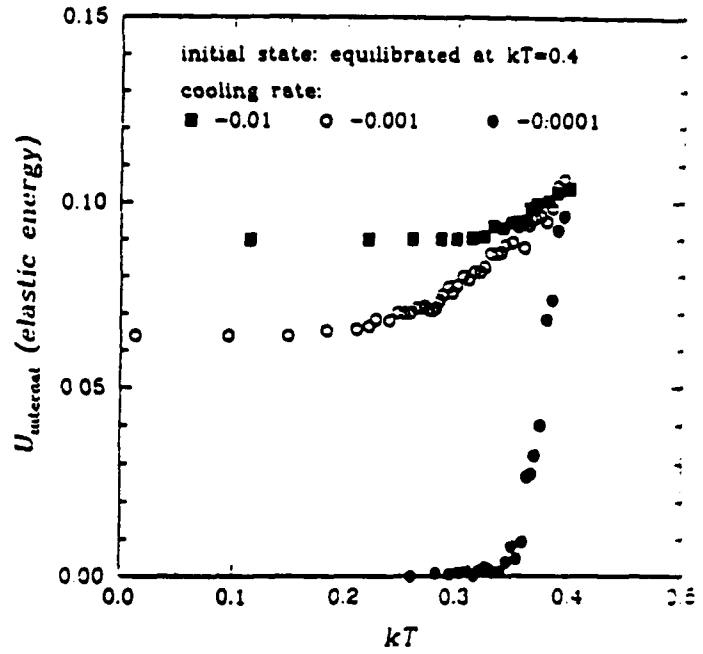
II-C-29

2. All the internal misfit stresses induced by LISTs are explicitly accounted for !!!

Equilibrium and kinetic properties at zero stress

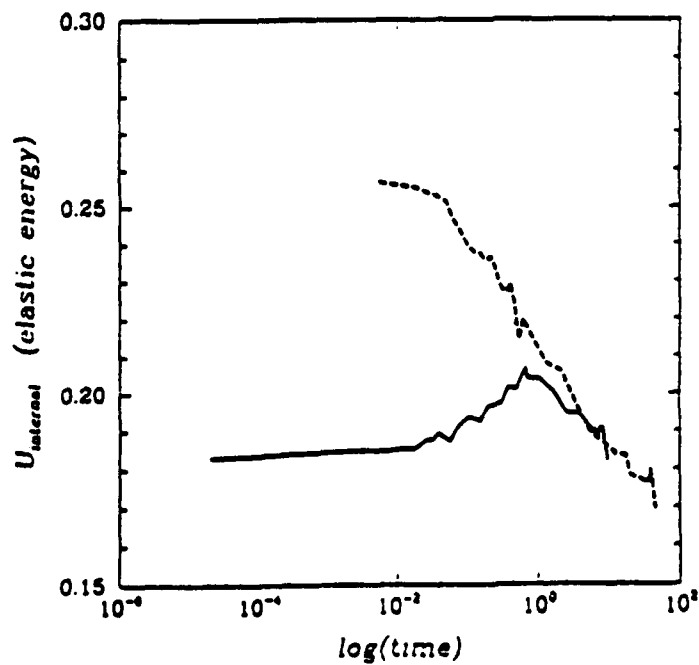


The equation of state

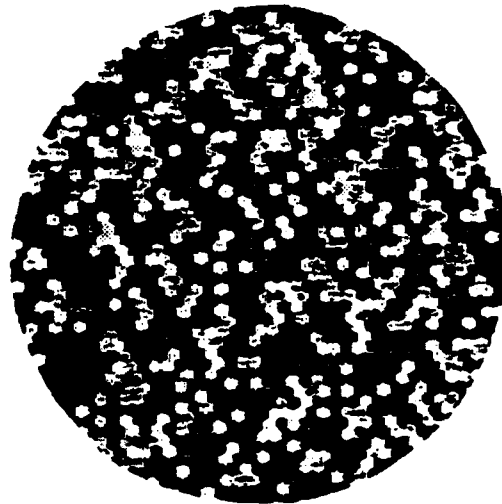
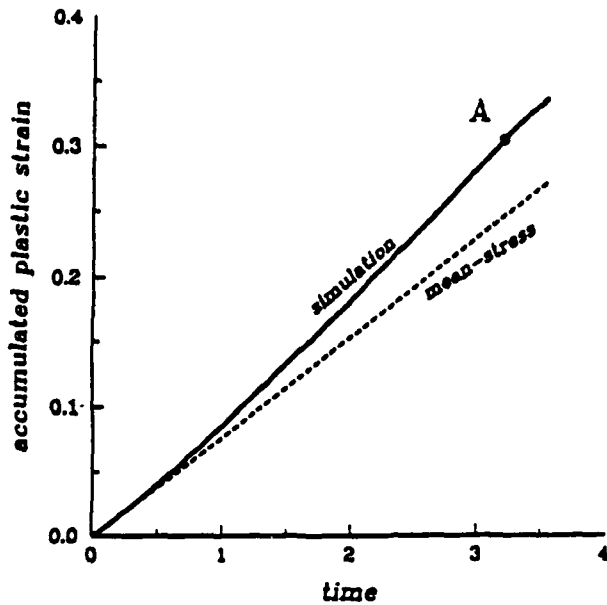


Cooling with different rates
simulations - "vitrification"

Memory effect (—) versus plain relaxation (---)

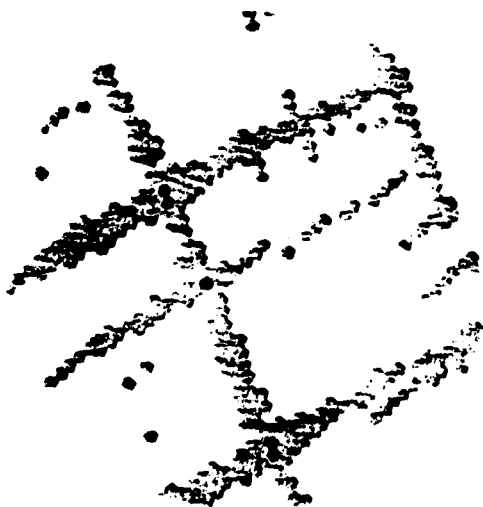


Transition to the localized flow at lower temperatures

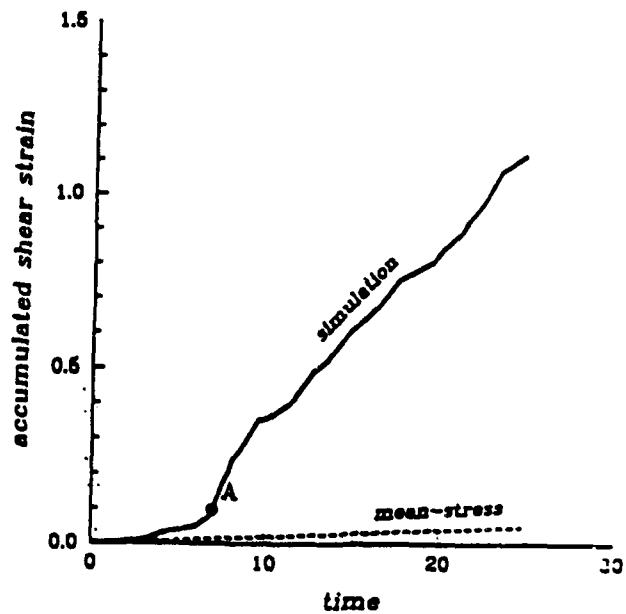


A typical configuration of the high temperature flow

($kT=2.0$, $\sigma=1.0$, initial state="no LITs").

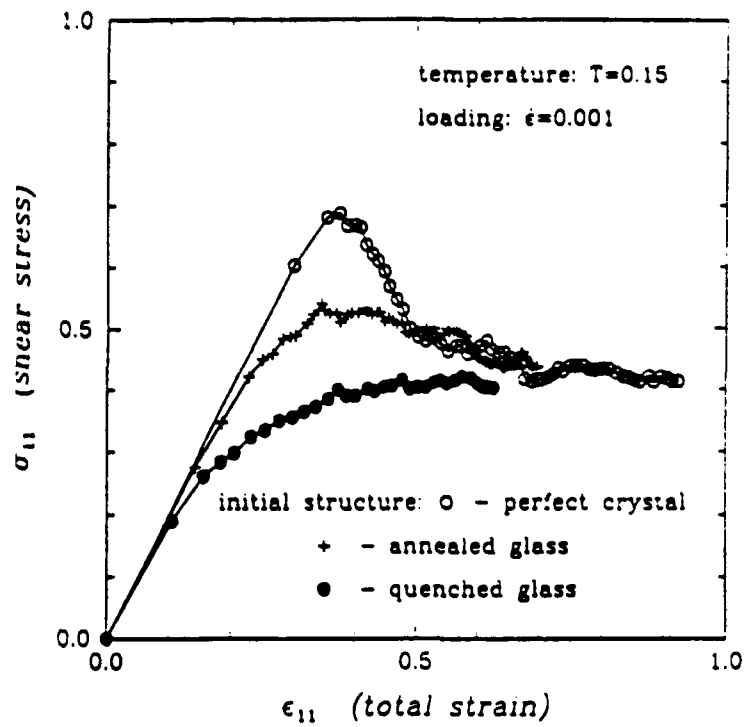


A typical configuration of the low temperature flow

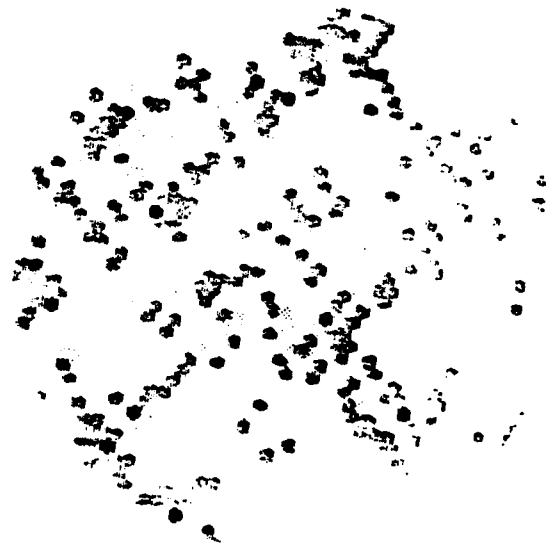
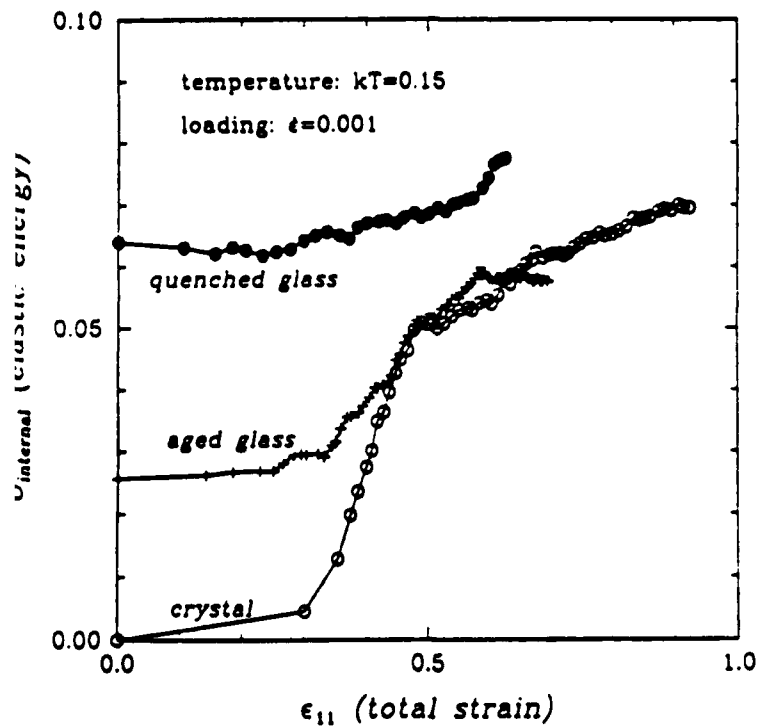


($kT=0.15$, $\sigma=1.0$, initial state="no LITs")

Effect of initial disorder on the flow pattern and kinetics

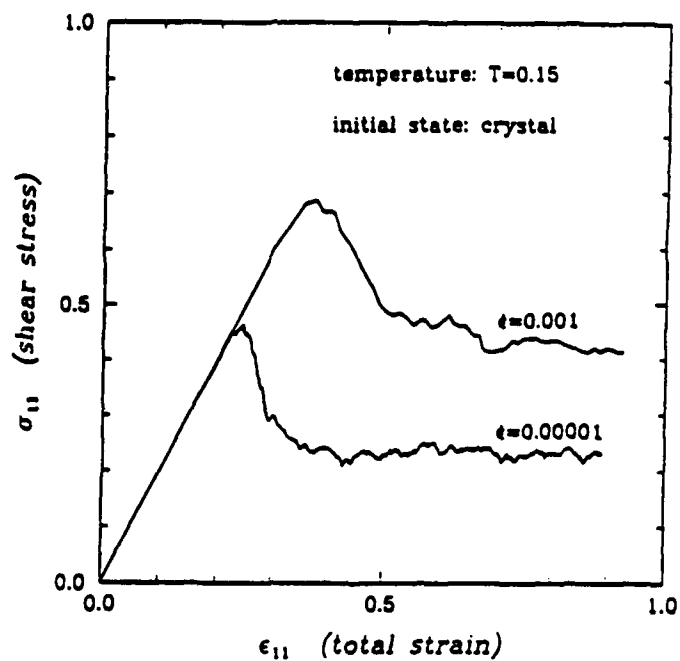


A typical configuration of the low temperature flow in crystal

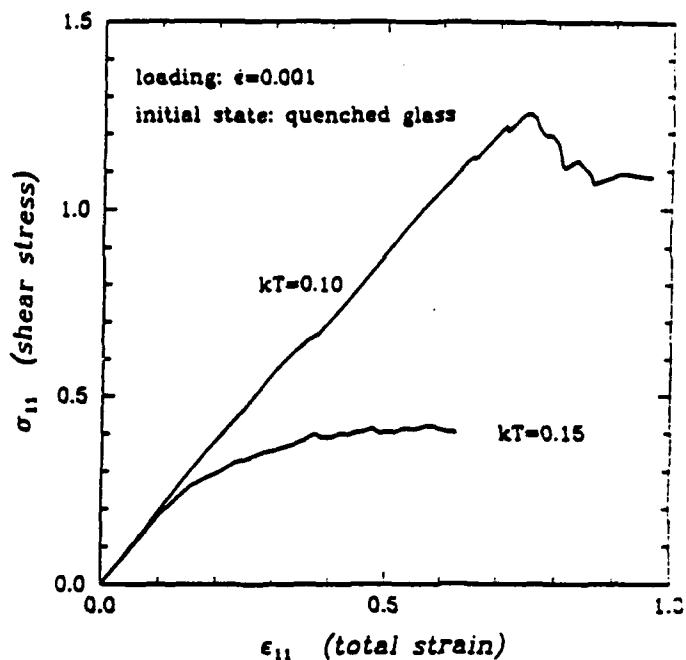


A typical configuration of the low temperature flow in glass

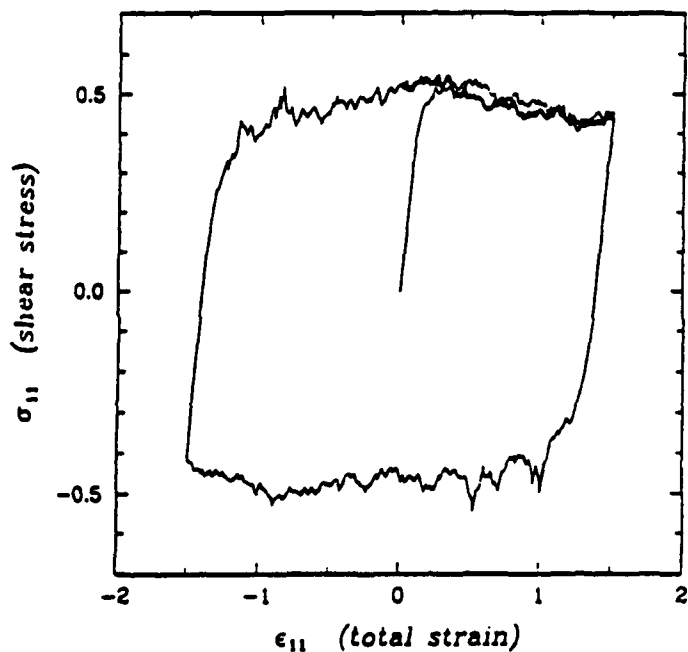
Constant strain rate simulations



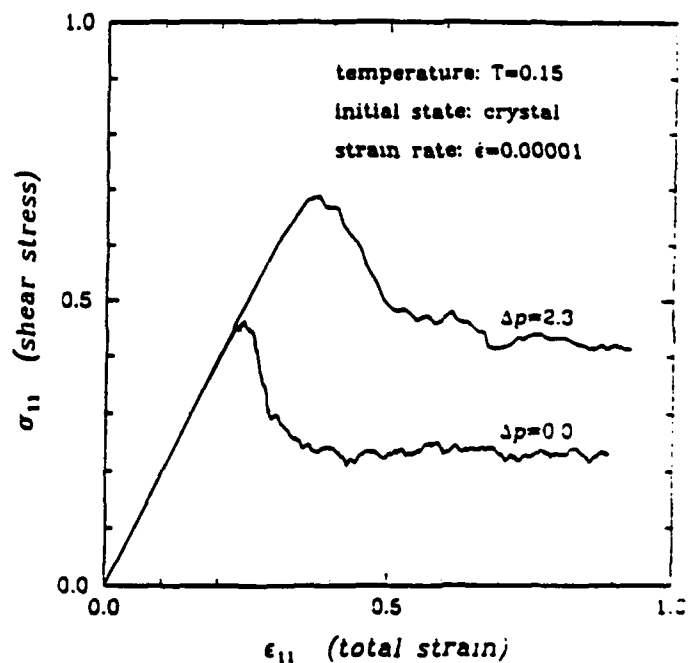
The strain rate effect



The temperature effect



Cyclic loading

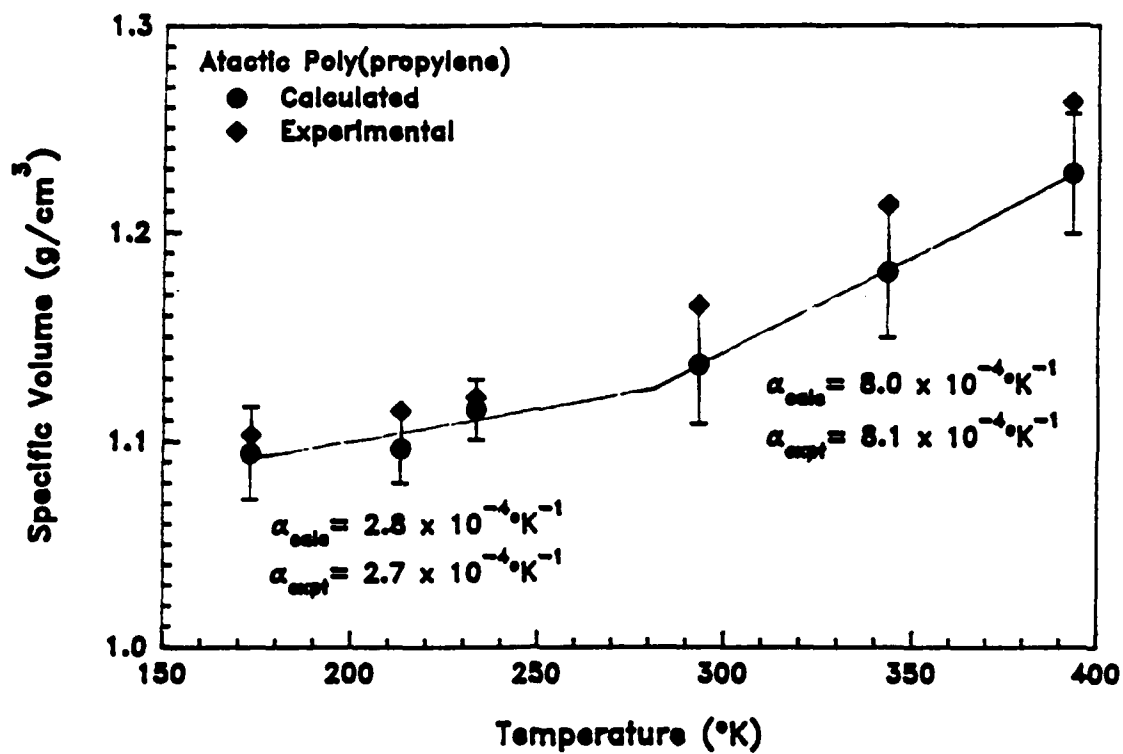


The pressure effect

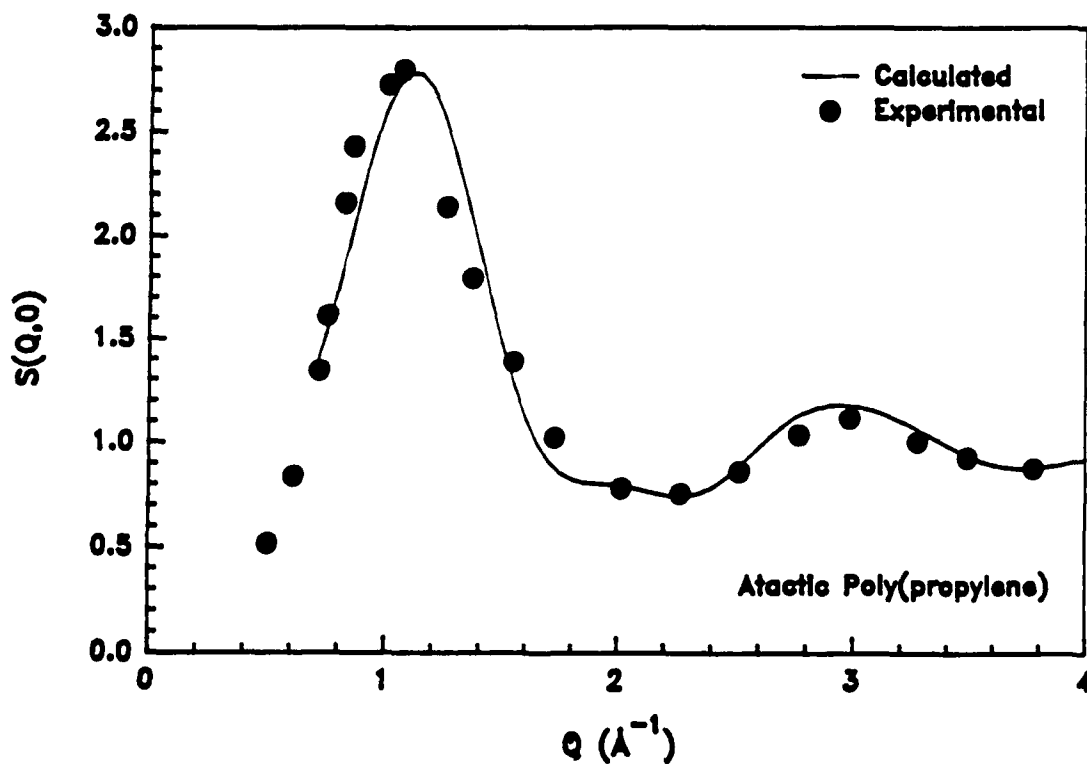
OVERVIEW OF ACCOMPLISHMENTS IN TASK II
(Yip, Argon, Bulatov, Deng, Sylvester)

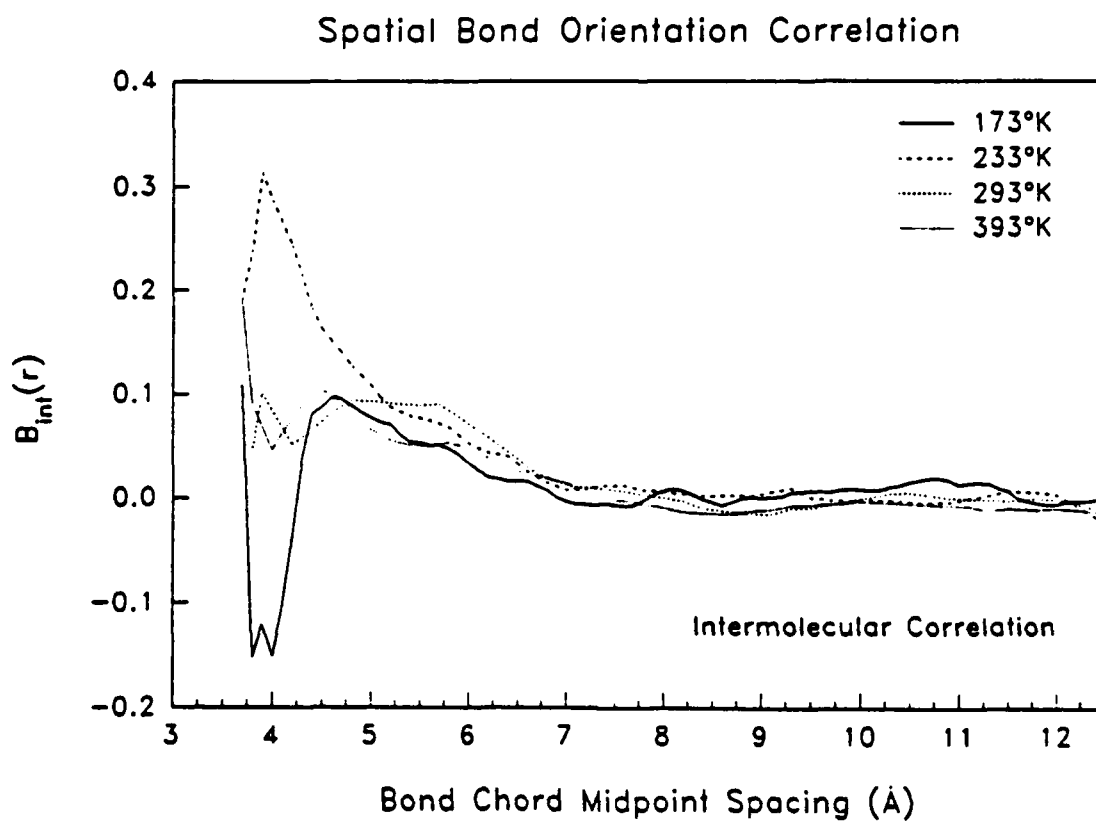
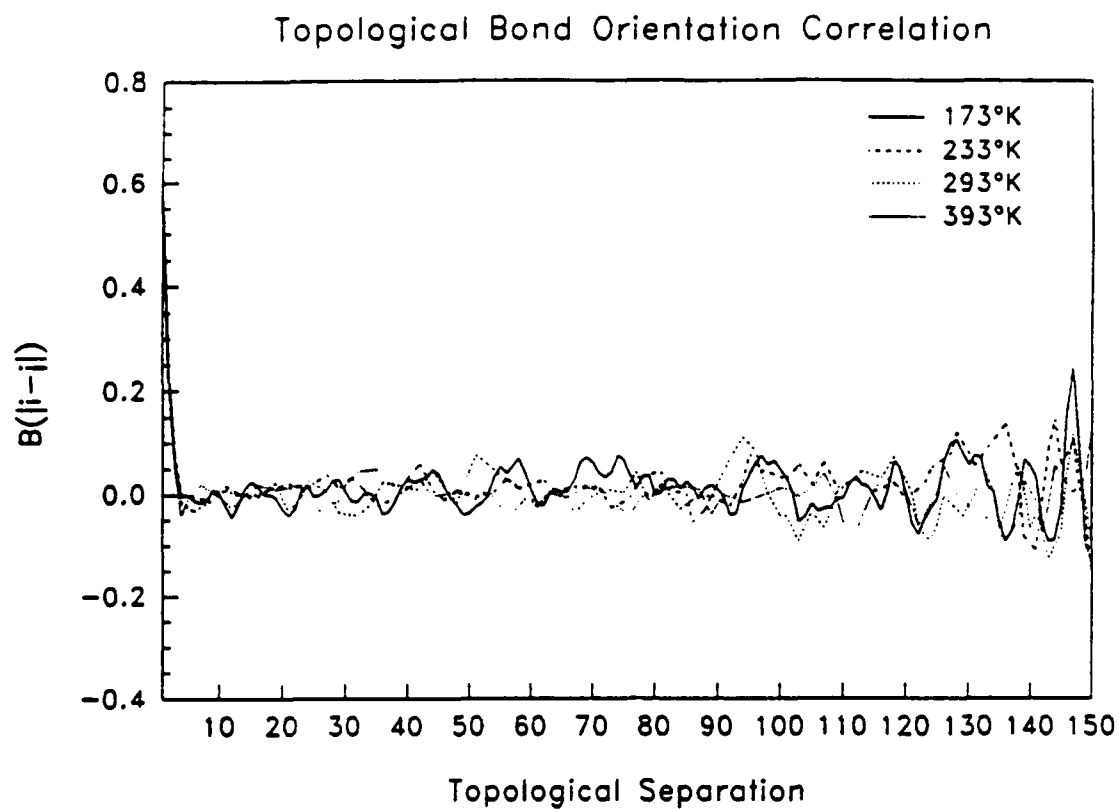
- o General molecular-dynamics model for dynamic simulations of structure and its relaxations in flexible chain glassy polymers
- o Simulation of structural relaxations by a combination of static energy minimization approaches and molecular dynamics based thermalization to probe segmental dynamic signatures of structure below and above the experimental glass transition temperature
- o Simulation of melting, quenching, and structural relaxations in 2-D atomic glass models
- o Simulation of the kinematics and kinetics of structure relaxations in 2-D models of amorphous elastic media

Specific Volume vs. Temperature

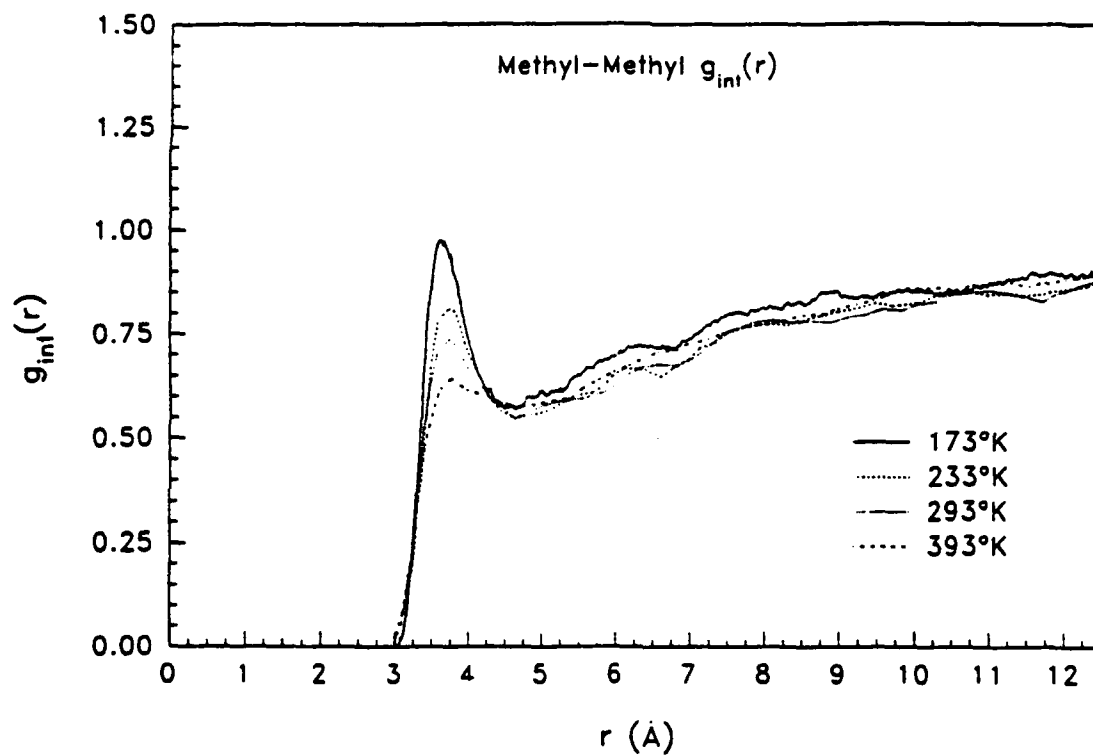


X-ray Structure Factor

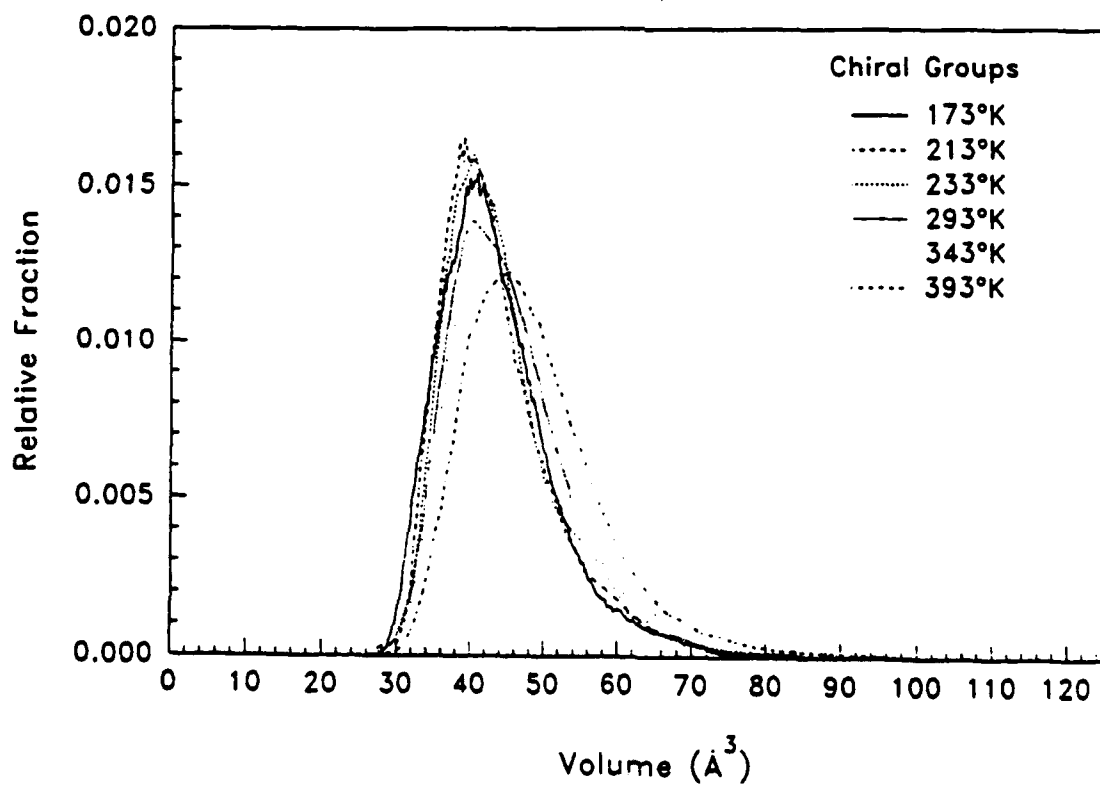


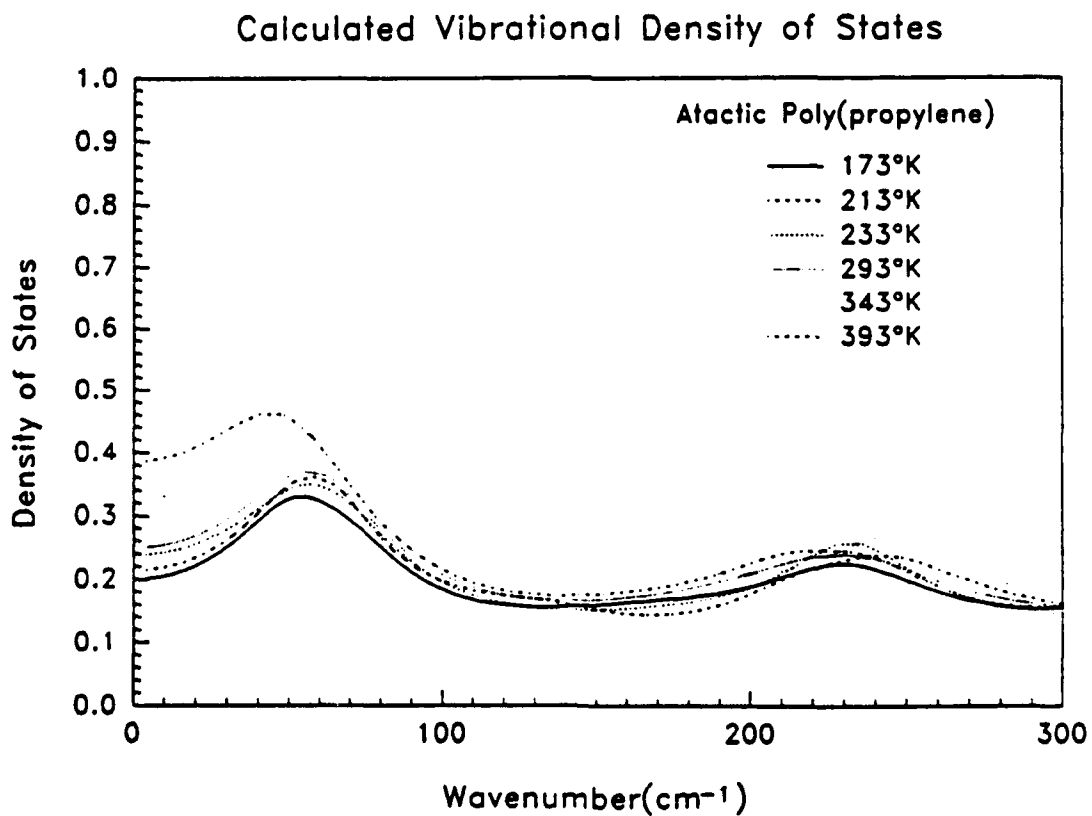
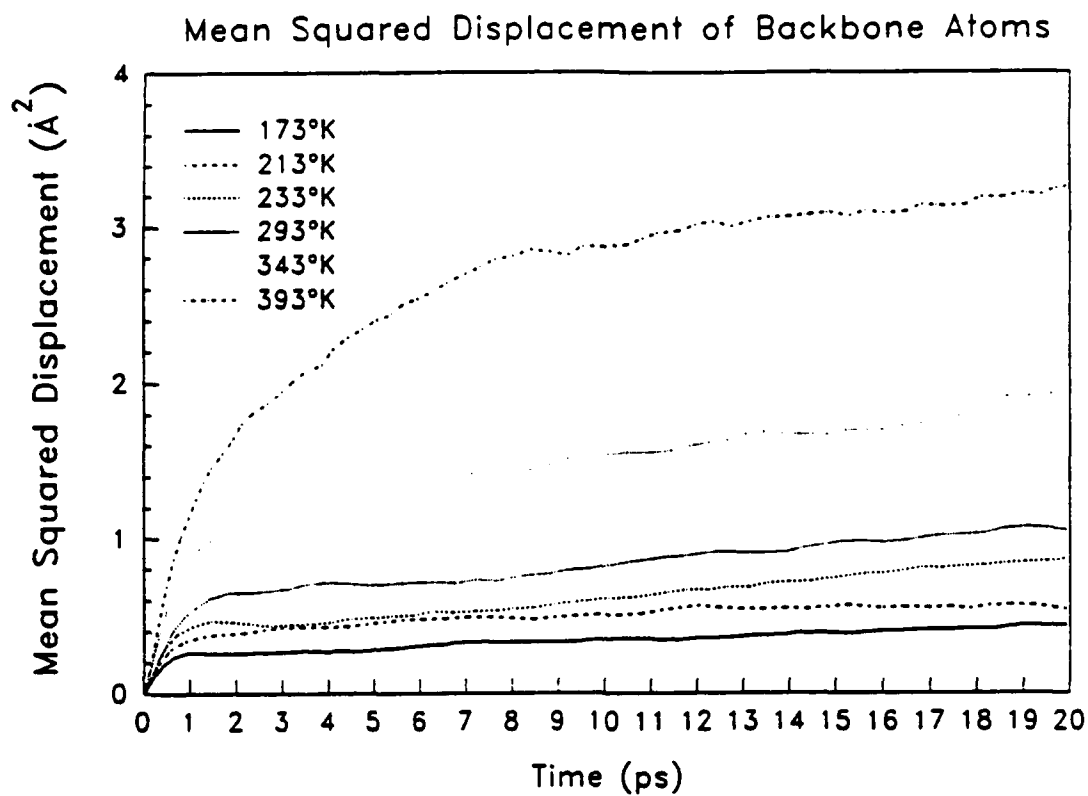


Intermolecular Pair Radial Distribution Function

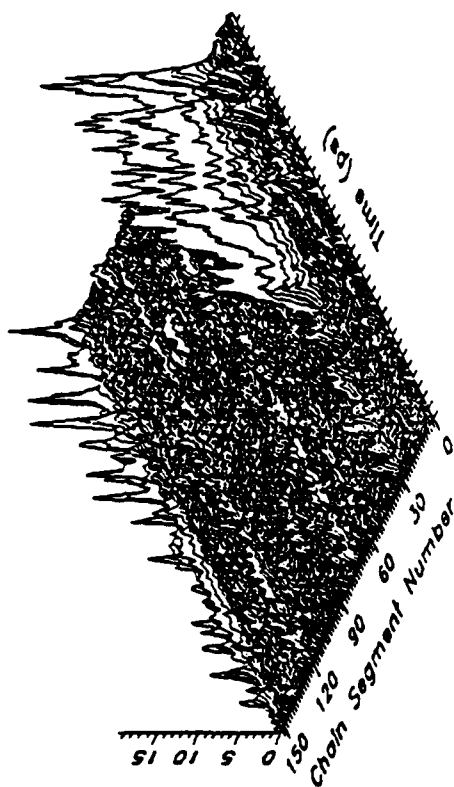


Distribution of Group Voronoi Volume

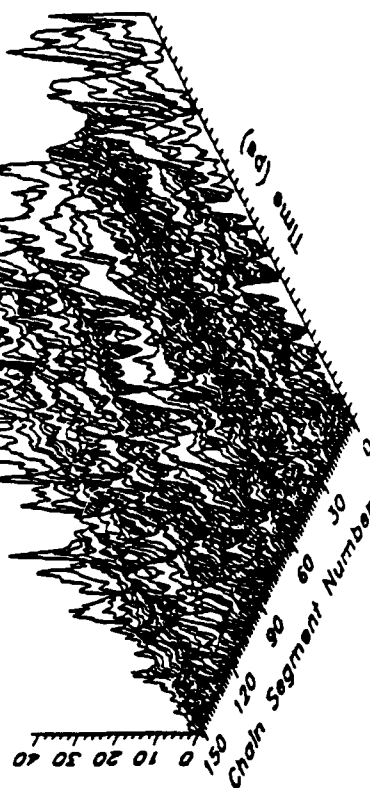




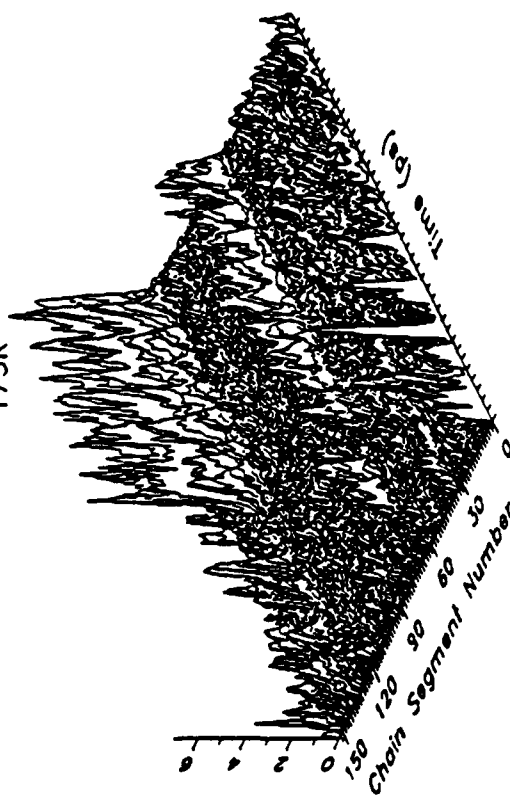
233K



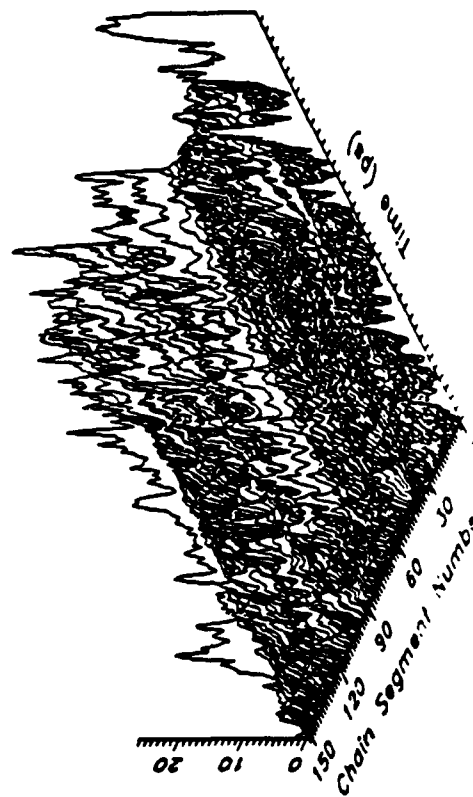
393K



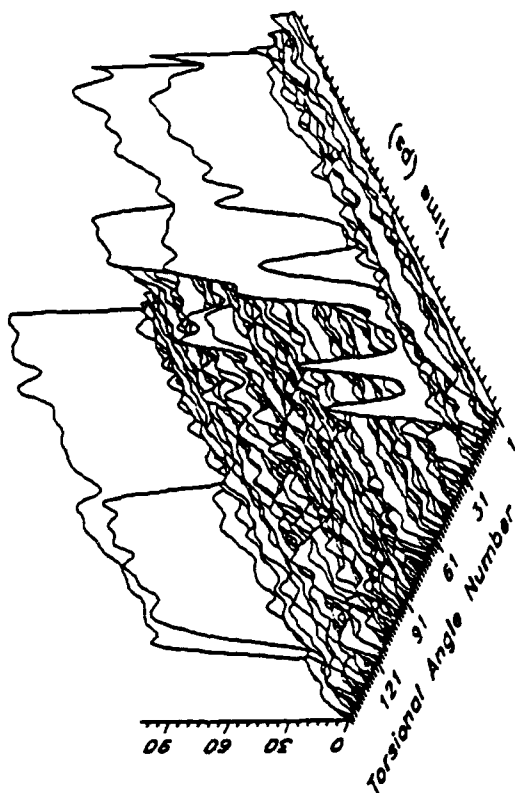
173K



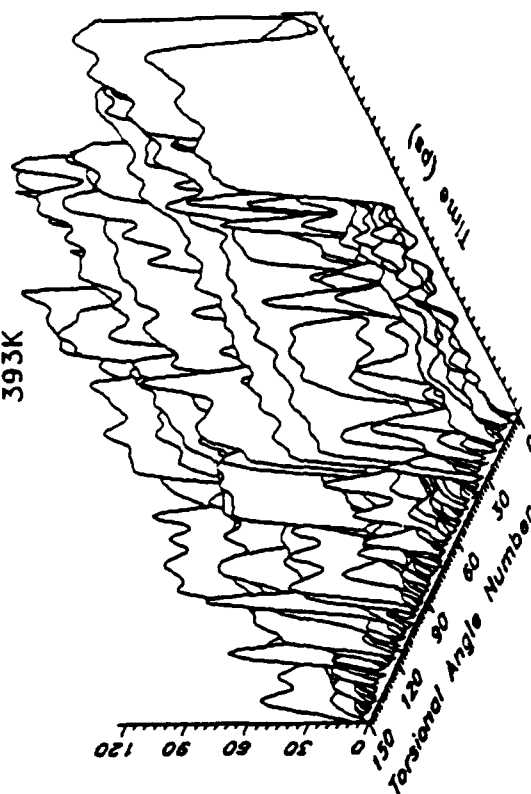
293K



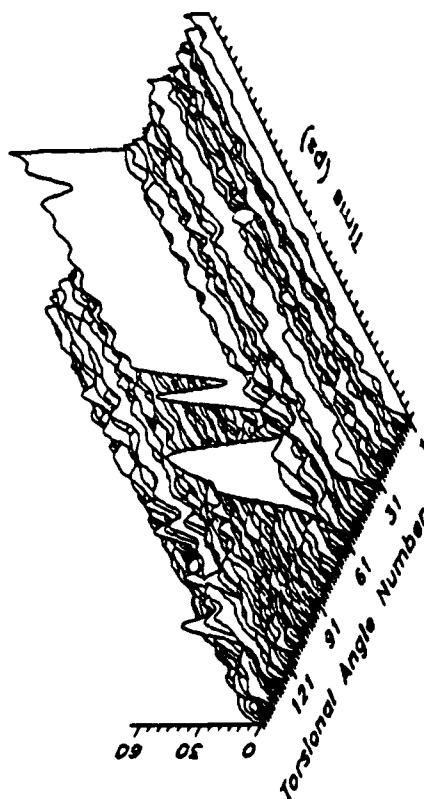
233K



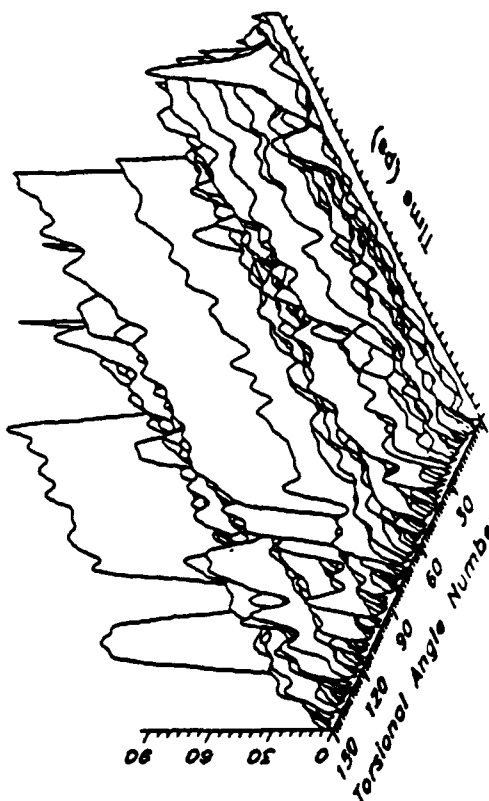
393K



173K



293K



OVERVIEW OF ACCOMPLISHMENTS IN TASK III

(Parks, Argon, Ahzi, Lee)

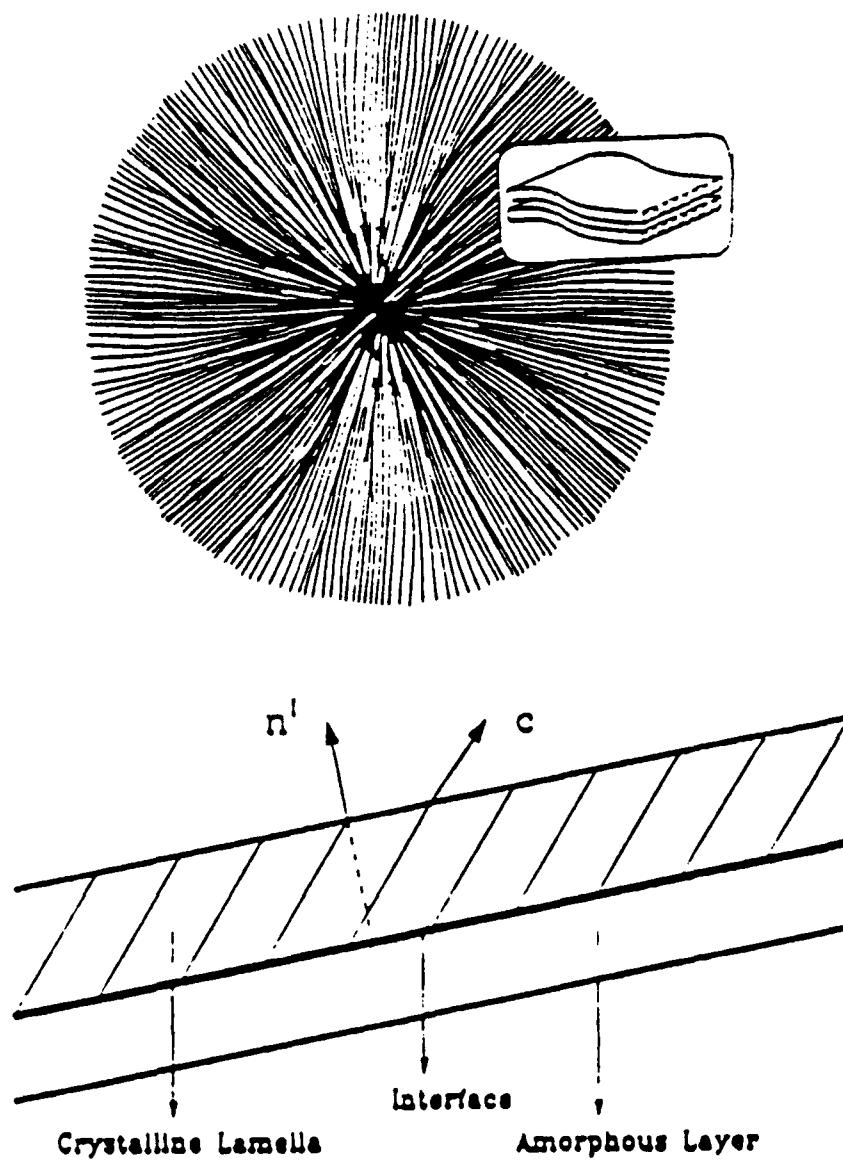
- o Constrained Hybrid (CH) model (100% crystalline lamellar solid, with a modified, upper-bound Taylor approach) for large strain deformation and texture development
- o Modified CH (Mod-CH) model with amorphous layers attached to lamellae
- o Simulations of texture development and stress-strain behavior, with both CH and Mod-CH models, and comparison with experiments for:
 - Uniaxial tension; uniaxial compression
 - Plane strain compression
 - Simple shear
- o Complementary Mod-CH model consisting of crystalline lamellae, with modified lower-bound Sachs approach. (still under development)

OVERVIEW OF ACCOMPLISHMENTS IN TASK IV

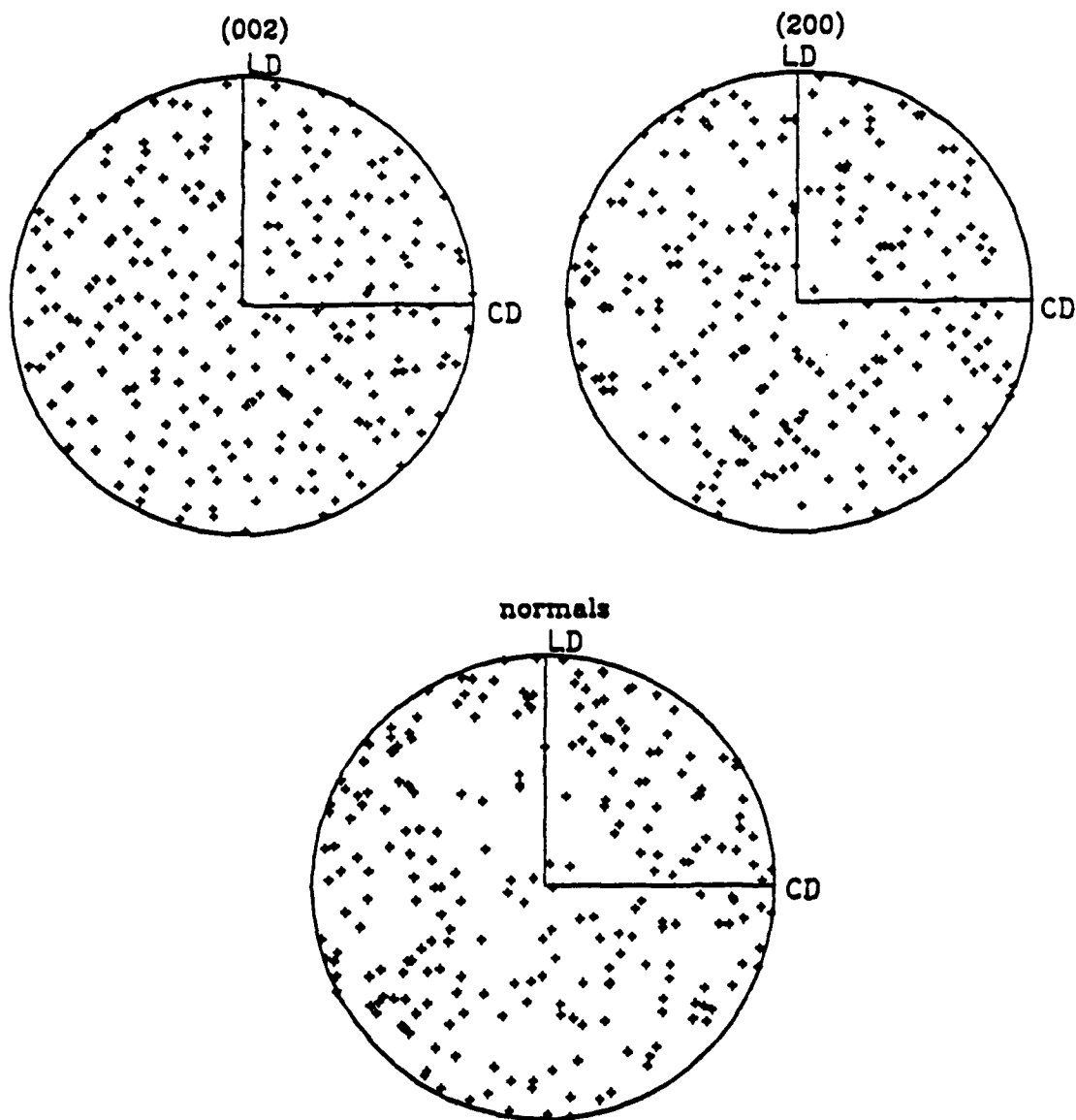
(Cohen, Argon, Anderson, Bellare, Bartczak, Galeski,
Lin, Song)

- o Texture evolution experiments combining measurements of stress-strain, density change, light microscopy, TEM, SEM, SAXS, WAXS in:
 - PE Plane strain compression
 - PE Uniaxial compression
 - PE Simple shear
 - Nylon-6 Plane strain compression
 - PET Plane strain compression
 - Isotactic PS Plane strain compression
- o Textural mechanical anisotropy measurements in:
 - Nylon-6 Elastic constants in orthotropic texture
 - PE Yield surface studies
 - Nylon-6 Yield surface studies
- o Thermal analysis of dislocation motion in simple shear deformation of highly textured Nylon-6, on the best chain slip plane

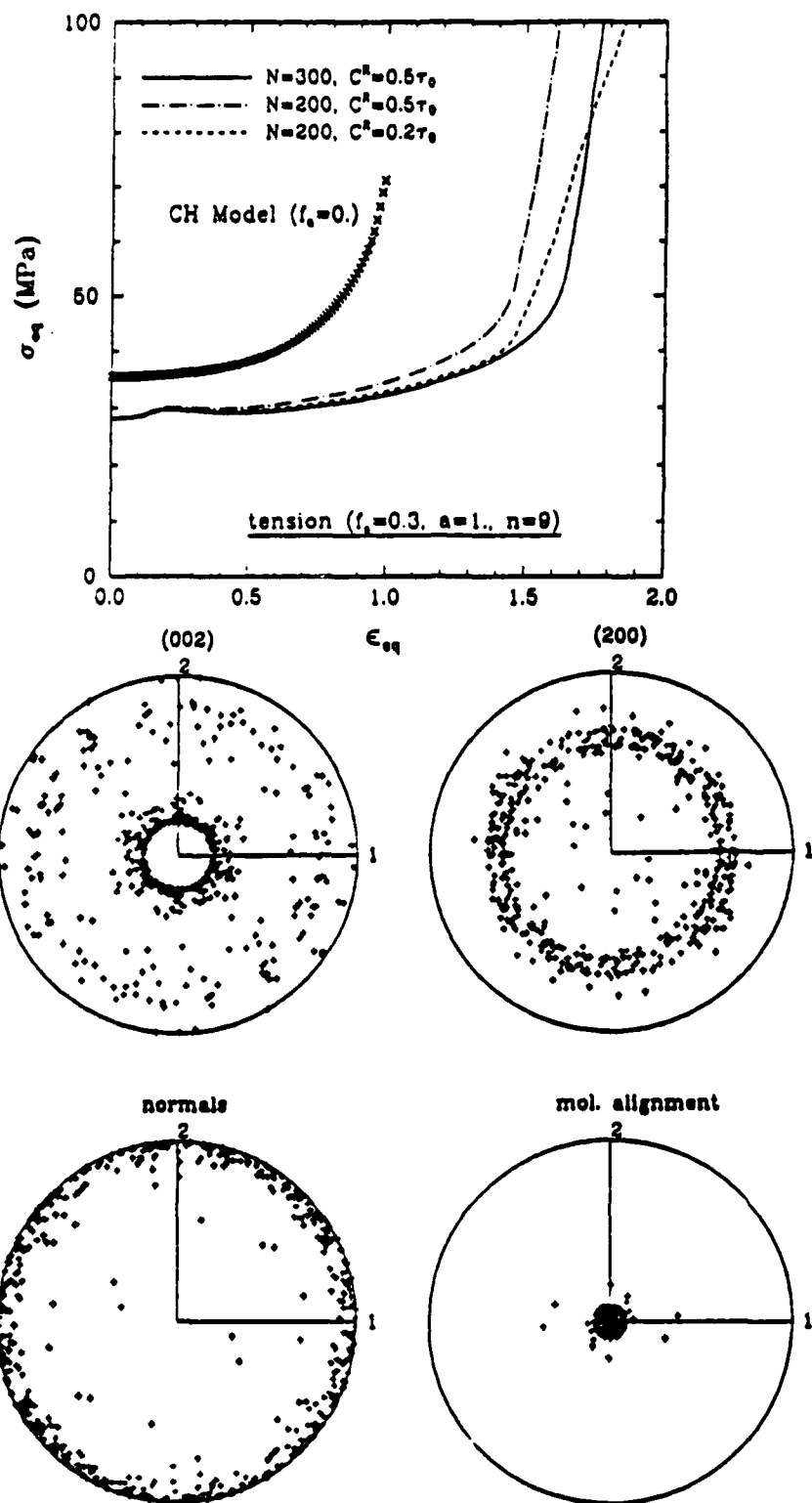
THE SEMI-CRYSTALLINE STRUCTURE MODEL



INITIAL ORIENTATION DISTRIBUTION

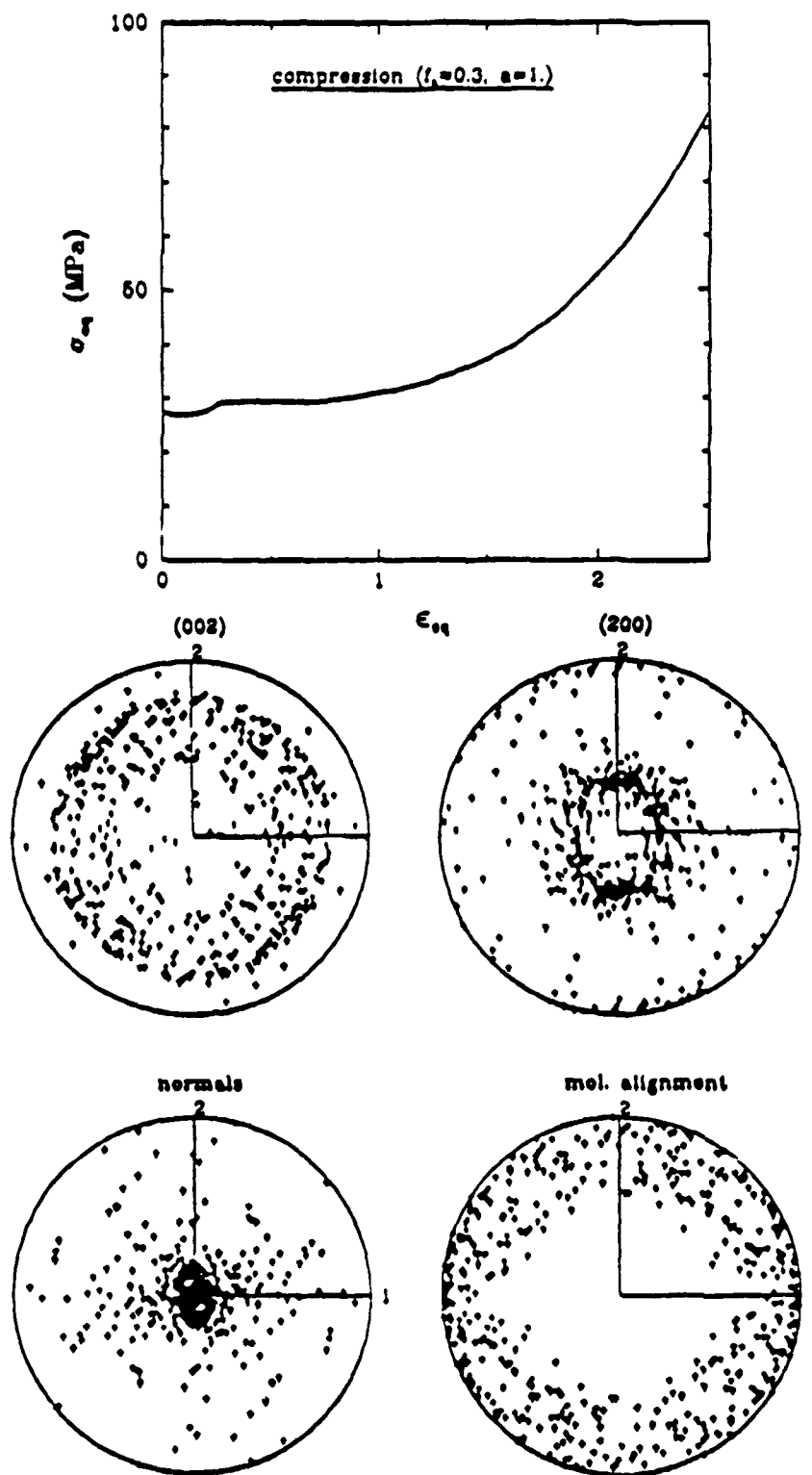


STRESS-STRAIN RESPONSE IN UNIAXIAL TENSION



POLW FIGURES REPRESENTING THE PREDICTED TEXTURE AT 170% TENSION
 IN THE 3 DIRECTION: CRYSTALLOGRAPHIC TEXTURE, LAMELLA NORMALS,
 MOLECULAR ALIGNMENT

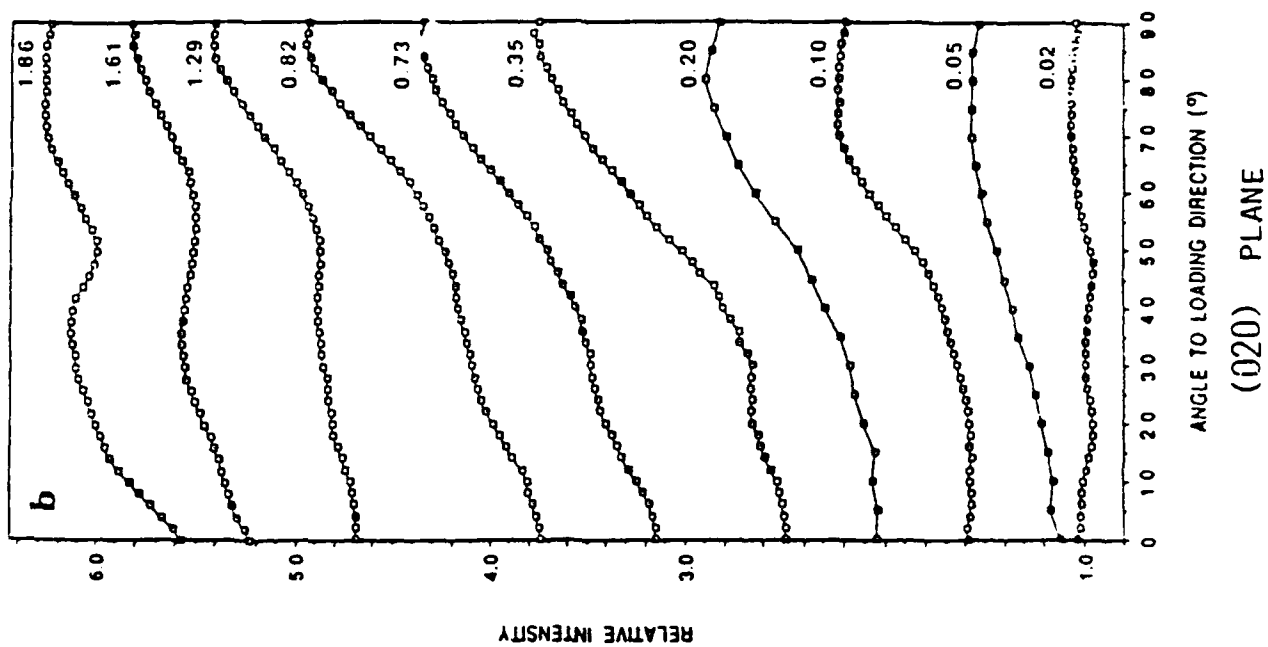
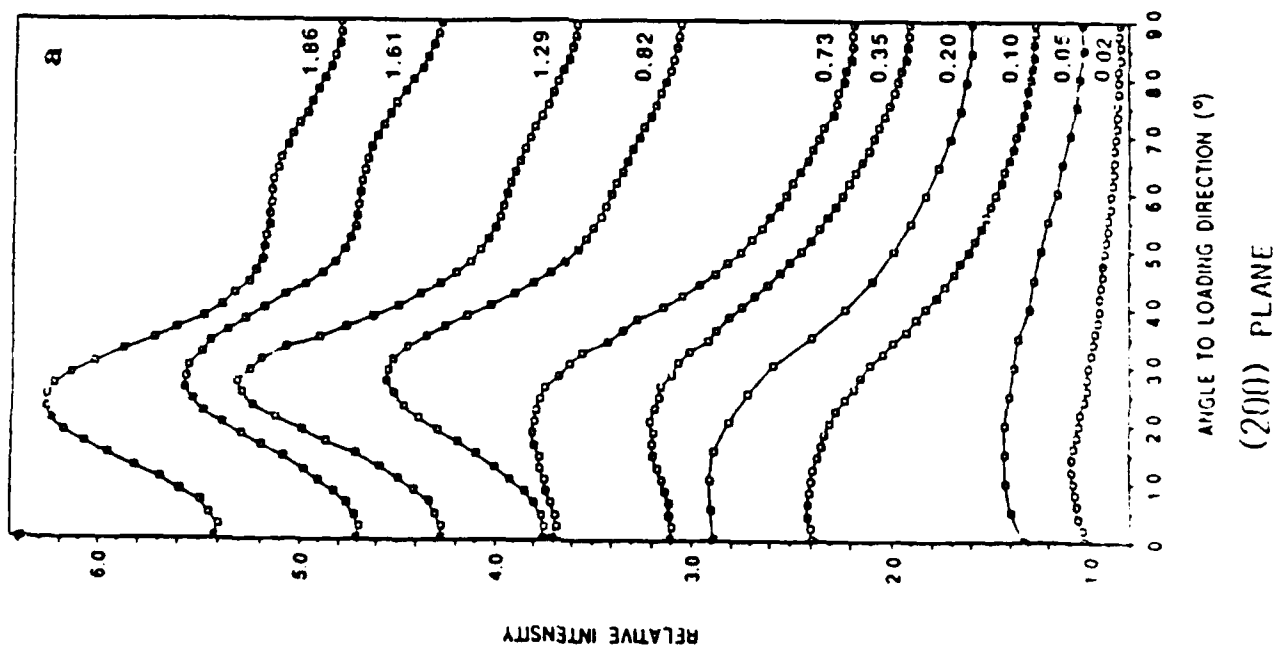
STRESS-STRAIN RESPONSE IN UNIAXIAL COMPRESSION



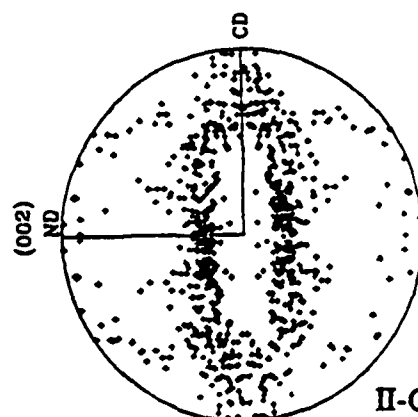
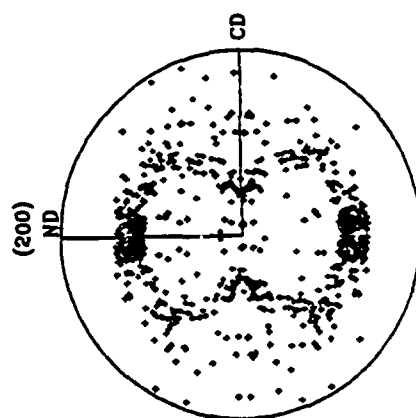
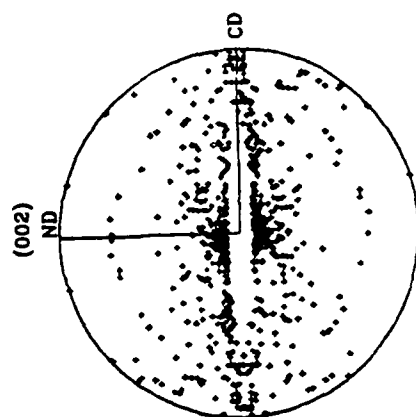
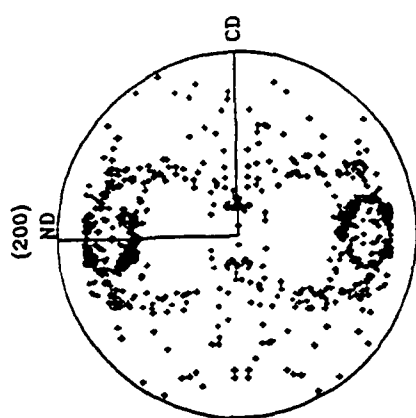
POLE FIGURES REPRESENTING THE PREDICTED TEXTURE AT 100% COMPRESSION IN THE 3 DIRECTION: CRYSTALLOGRAPHIC TEXTURE; LAMMELLA NORMALS DISTRIBUTION AND MOLECULAR ALIGNMENT

CHANGES IN THE ALTITUDE ANGLE DISTRIBUTION OF THE WAXS INTENSITIES WITH COMPRESSIVE

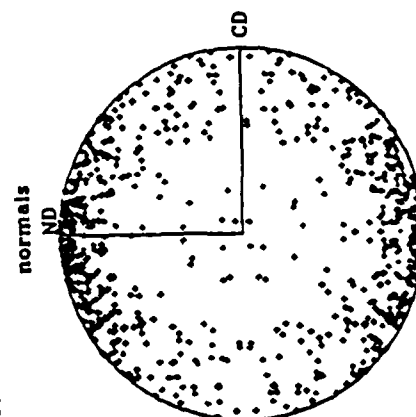
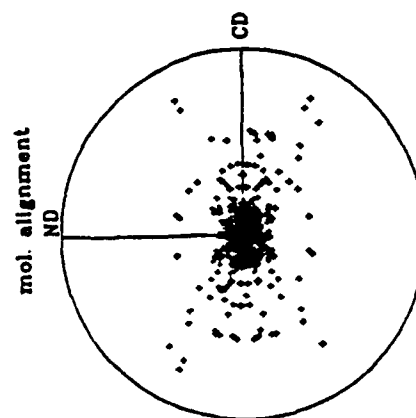
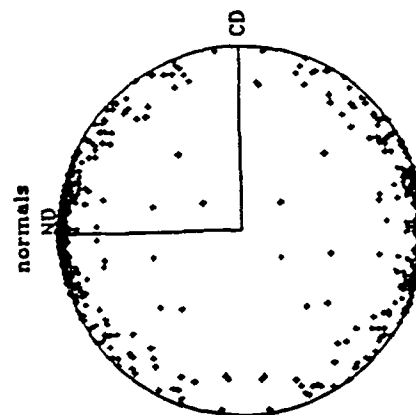
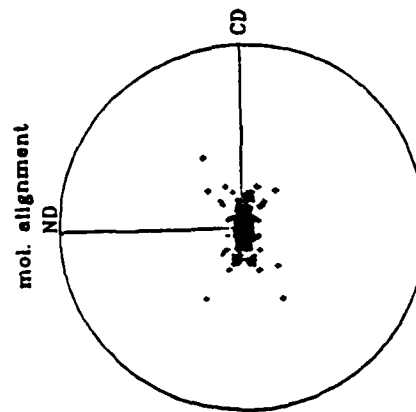
STRAIN



PREDICTED POLE FIGURE TEXTURES FOR PLANE STRAIN COMPRESSION



II-C-48

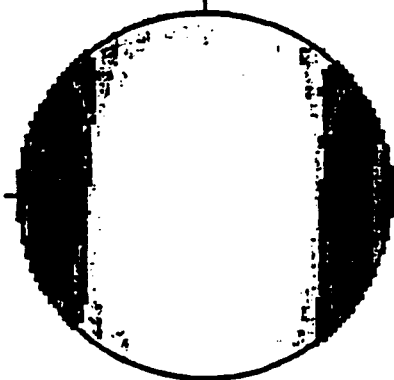


180% COMPRESSION

100% COMPRESSION

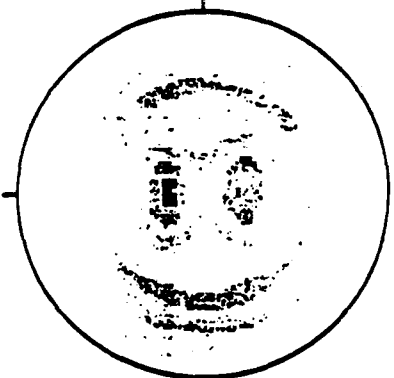
EXPERIMENTAL PLANE STRAIN COMPRESSION TEXTURES

(2 0 0)



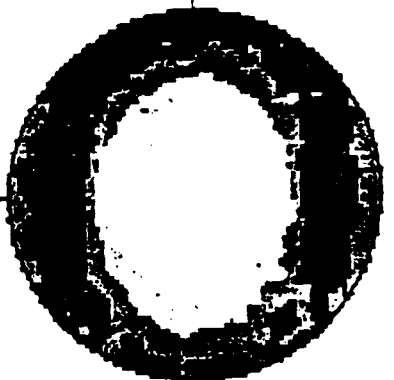
COMPRESSION RATIO 2.5

(0 0 2)



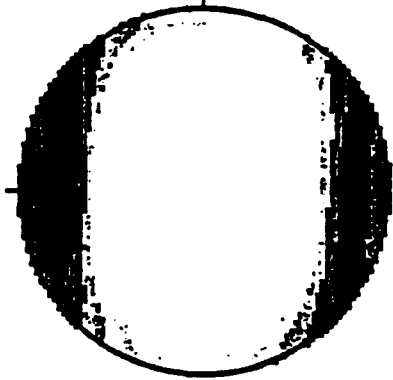
COMPRESSION RATIO 2.5

ANISOTROPY, $\Delta\rho/\rho$

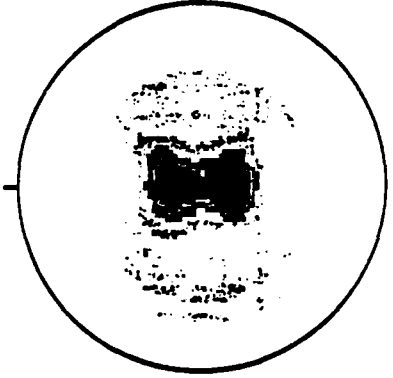


COMPRESSION RATIO 2.5

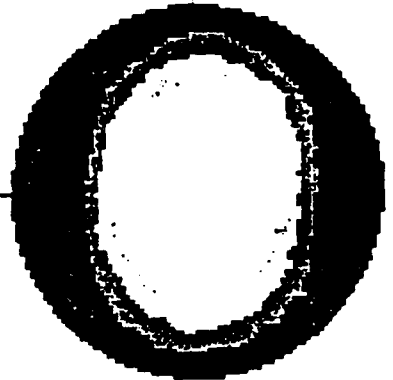
COMPRESSION RATIO 3.13



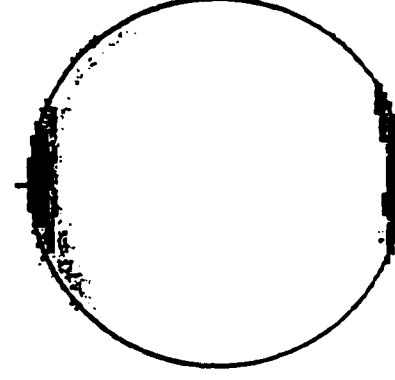
COMPRESSION RATIO 3.13



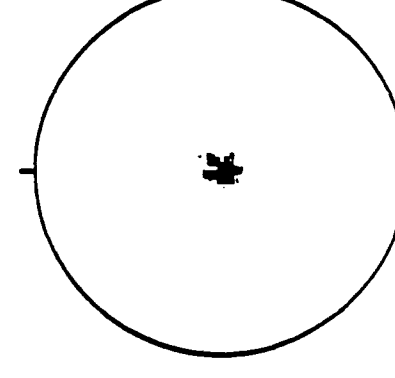
COMPRESSION RATIO 3.13



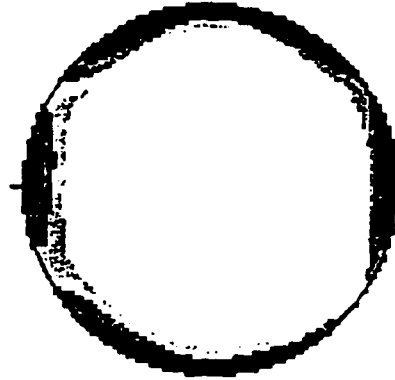
COMPRESSION RATIO 6.00



COMPRESSION RATIO 6.00



COMPRESSION RATIO 6.00

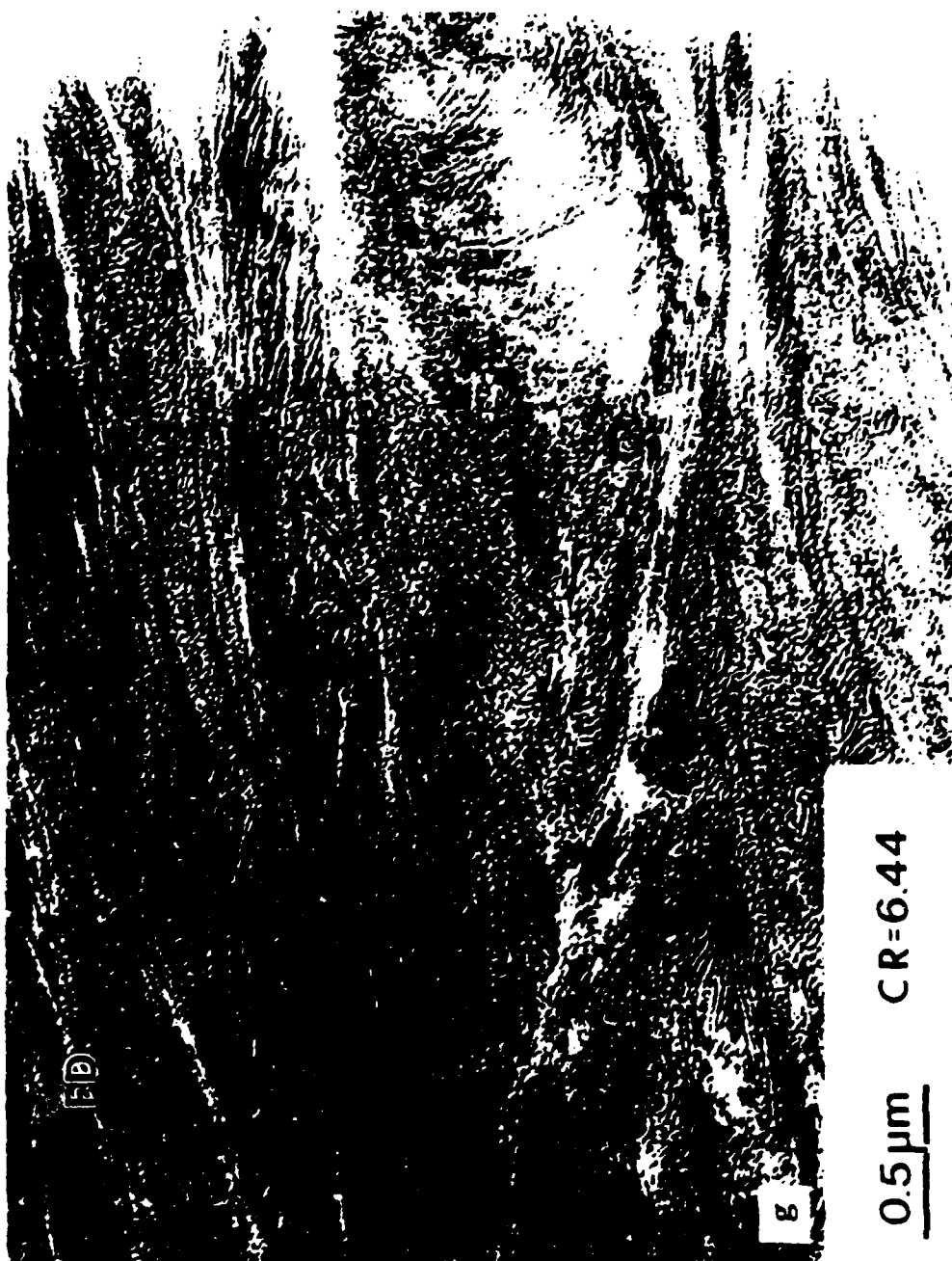




II-C-50



II-C-51



II-C-52

LD



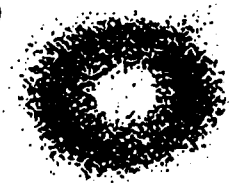
FD



LD



CR = 1.55



II-C-53

CR = 1.8



CR = 4.16



CR = 6.44



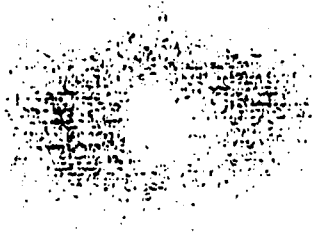
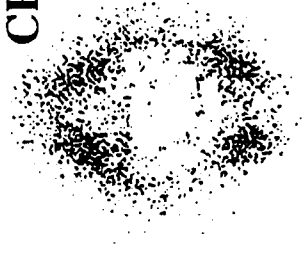
FD

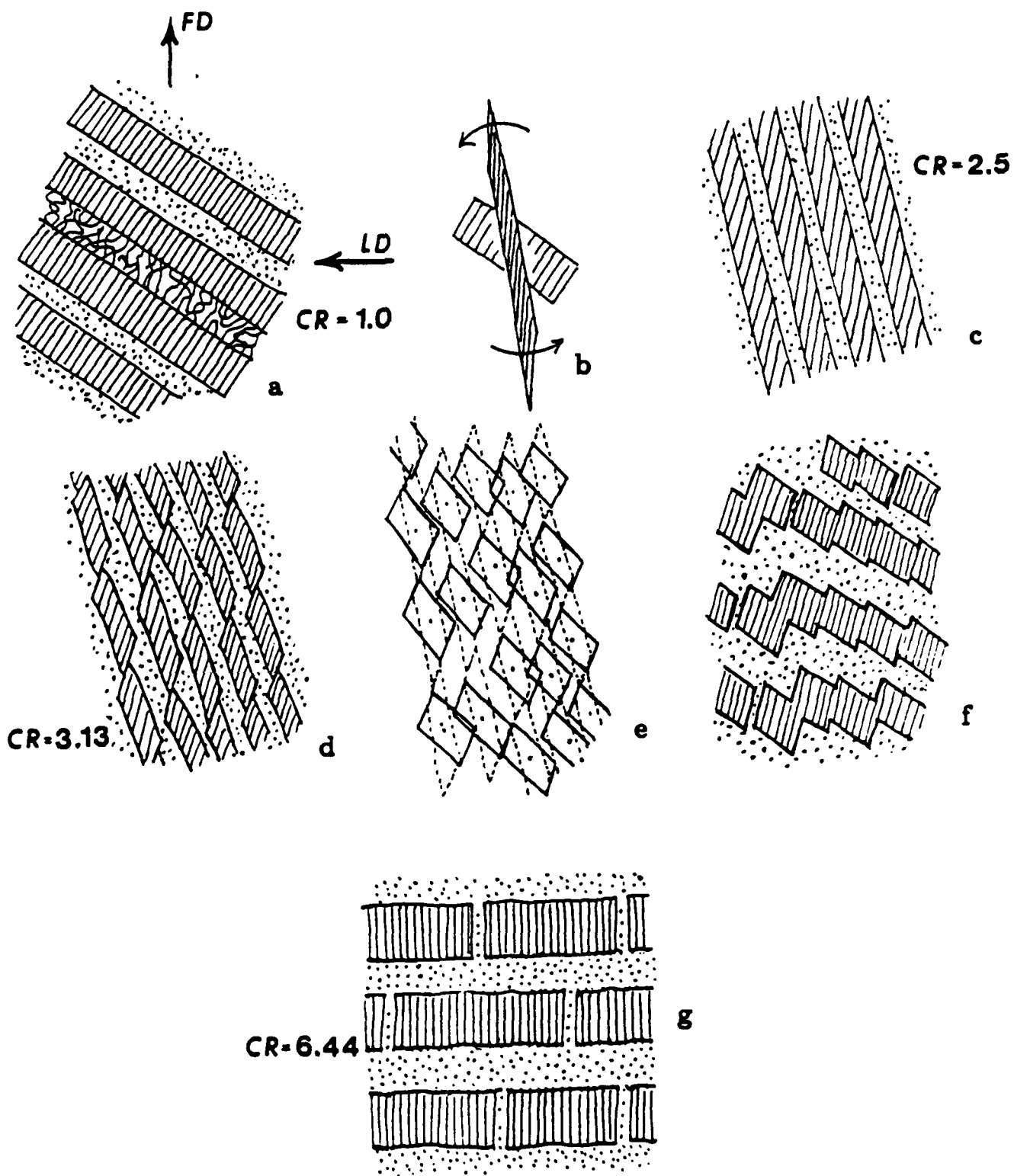


LD

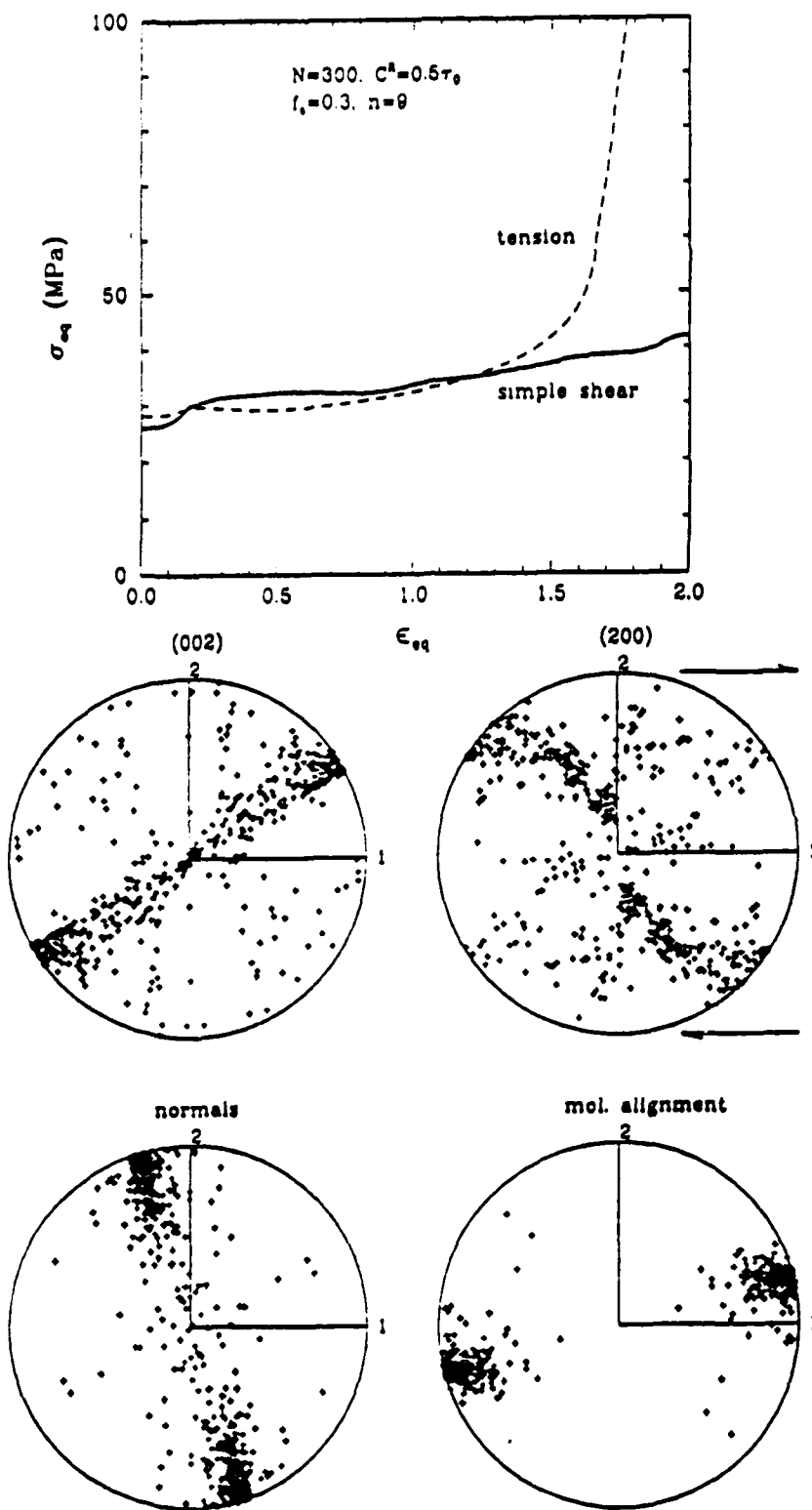


CR = 3.13





STRESS-STRAIN RESPONSE IN SIMPLE SHEAR

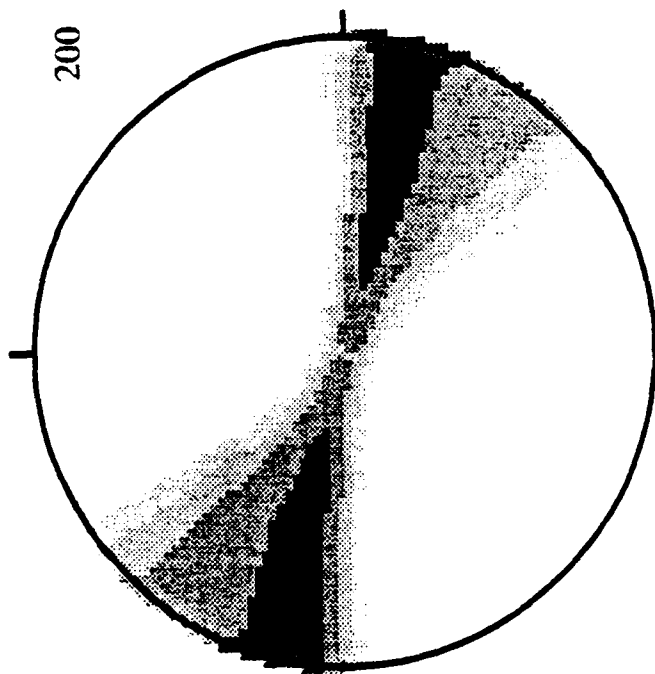
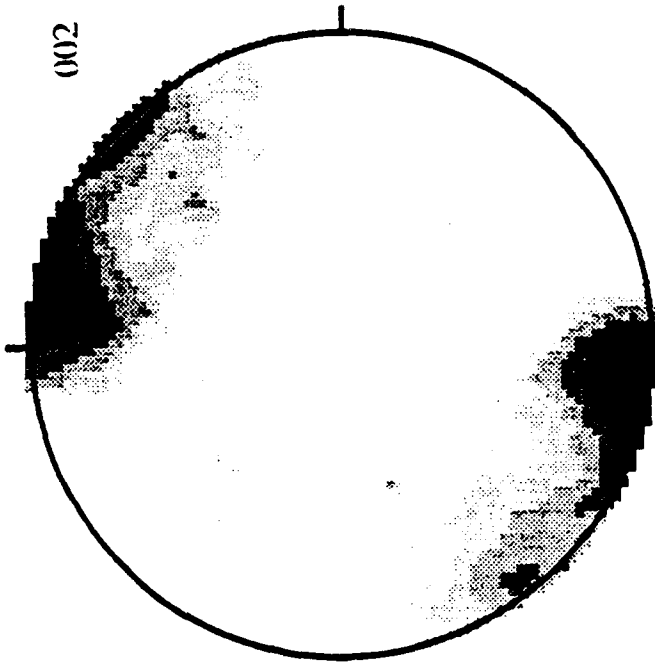


POLE FIGURES REPRESENTING THE PREDICTED TEXTURE FOR SIMPLE SHEAR $\gamma = 3.46$: CRYSTALLOGRAPHIC TEXTURE, LAMELLA NORMALS, AND

MOLECULAR ALIGNMENT

II-C-55

EXPERIMENTAL SIMPLE SHEAR TEXTURE AT $\gamma = 3.0$



8.00
5.50
3.78
2.60
1.79
1.23
0.85
0.58
0.40

II-C-56

(0 0 2)

(2 0 0)

USE OF ALLIANT COMPUTER FACILITY BENEFITING OTHER RESEARCH PROGRAMS

1. "Computer Simulation of Plastic Deformation in Glassy Polymers," Argon and Suter, NSF/DMR Grant DMR-8517224, work in progress.
2. "Modeling Intergranular Creep Damage Distribution at the Tips of Cracks and Notches in Single Phase Alloys," Argon and Parks, NSF/MRL Grant 84-18718, submitted to Mechanics of Materials.
3. "Modeling Inhomogeneous Creep Deformation in Two-Phase Ordered Superalloys," Argon, NSF/MRL Grant 84-18718, work in progress.
4. "Simulation of Laser Pulse Generated Spallation of Protective Coatings from Substrates," Argon, Parks and Cornie, ONR Contract N00014-84-K, work in progress.
5. "Modeling Crack Tip Decohesion in Brittle Cleavage Fracture," Argon and Parks, DOE Grant DE-FG02-85ER13335, work in progress.
6. "Closed Loop Control of Sheet Forming Processes," Hardt and Boyce, NSF Mfg. Systems Program.

7. "Mechanics of Glassy Polymers During Solid Phase Processing," Boyce, NSF Materials Processing.
8. "Void Nucleation in Nonlinear Solid Mechanics," Abeyaratne, U.S. Army Research Office, DAAL 03-87-K-0016.
9. "Fundamentals of Elastic-Plastic Fracture," Parks and McClintock, DOE Grant DE-FR02-85ER13331.
10. "Mechanisms of Transformation Toughening," Parks and Olson, Subcontract from Northeastern University; DOE.
11. "Engineering Sciences of Solids Comminution," Peterson and McClintock, DOE Grant DE-FR02-85FR1331.
12. "Microstructural Evolution in Two-Phase Ordered Superalloys," Parks, NSF/MRL Grant DMR-84-18718.
13. "Experimental Plasticity," Anand, Office of Naval Research Contract No. N00014-86-K-0308.
14. "Experimental and Computational Study of Flow Localization and Ductile Fracture at High Temperatures, with Application to Hot Workability, Anand and Parks, NSF Grant No. MSM-99-O-8556.

USE OF WAXS AND SAXS X-RAY FACILITY BENEFITING OTHER RESEARCH PROGRAMS

1. "Spatial Arrangement in Block Domains in Di-Block Copolymers," Cohen and Berney, Bayer Professorship of Cohen. (SAXS Studies)
2. "Synthesis of PB-iPS Di-Block Copolymers," Cohen, ONR Contract N00014-87-K-0517. (SAXS Studies)
3. "Texture Development in Uniaxially Deformed Nylon 6," Galeski, Cohen, Argon, NSF/MRL Grant 87-18718. (WAXS Studies)
4. "Orientation in Polyaramid Fibers," Suter, ONR Contract . (WAXS Studies)
5. "Liquid Crystalline Domains in a Series of Polyimides," Cebe (unsupported). (SAXS Studies)
6. "Gas Permeation in Block Copolymer Membranes," Cohen, Baddour Lamott DuPont Professorship. (SAXS Studies)
7. "Synthesis of Nylon 6-Polyisoprene Di-Block Copolymers," Cohen, Argon, NSF/MRL Grant 87-18718. (SAXS & WAXS Studies)
8. "Texture Development in Nylon 6," Argon, NSF/MRL Grant 87-18718. (WAXS & SAXS Studies)
9. "Domain Ordering in Di-Block Copolymers," Cohen, Berney, ONR Contract N00014-87-K-0517. (SAXS Studies)

UNIVERSITY OF TEXAS AT ARLINGTON

Professor Martin Pomerantz



ELECTRONIC AND IONIC TRANSPORT IN PROCESSABLE CONDUCTING POLYMERS

**CENTER FOR ADVANCED POLYMER RESEARCH
DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF TEXAS AT ARLINGTON**

Martin Pomerantz, Organic/Polymer Chemistry

John R. Reynolds, Polymer Chemistry

Krishnan Rajeshwar, Electrochemistry

Dennis S. Marynick, Theoretical Chemistry

DOCTORAL PROGRAM IN **APPLIED CHEMISTRY**

- **Course Work**

- ◆ **Core Chemistry Courses**
- ◆ **Polymer Courses**
- ◆ **Industrial Chemistry Courses**

- **Industrial Internship**

- ◆ **General Dynamics**
- ◆ **Texas Instruments**
- ◆ **IBM**
- ◆ **Rockwell International**
- ◆ **Mobil Laboratories**
- ◆ **LTV Aerospace and Defense Co.**
- ◆ **Johnson and Johnson**
- ◆ **Exxon**
- ◆ **Shell**
- ◆ **Polytronix**
- ◆ **Alcon Laboratories**

- **Doctoral Research/Dissertation**

September, 1986 – December, 1991

- Many New State-of-the-Art Instruments for the Polymer Program

- ◆ Totals

- ▼ DARPA \$668,000

- ▼ UTA/TEXAS \$1,345,000

- Since January, 1986 UTA Chemistry Dept. has added over \$2.5 million in capital equipment

- New Chemistry Building

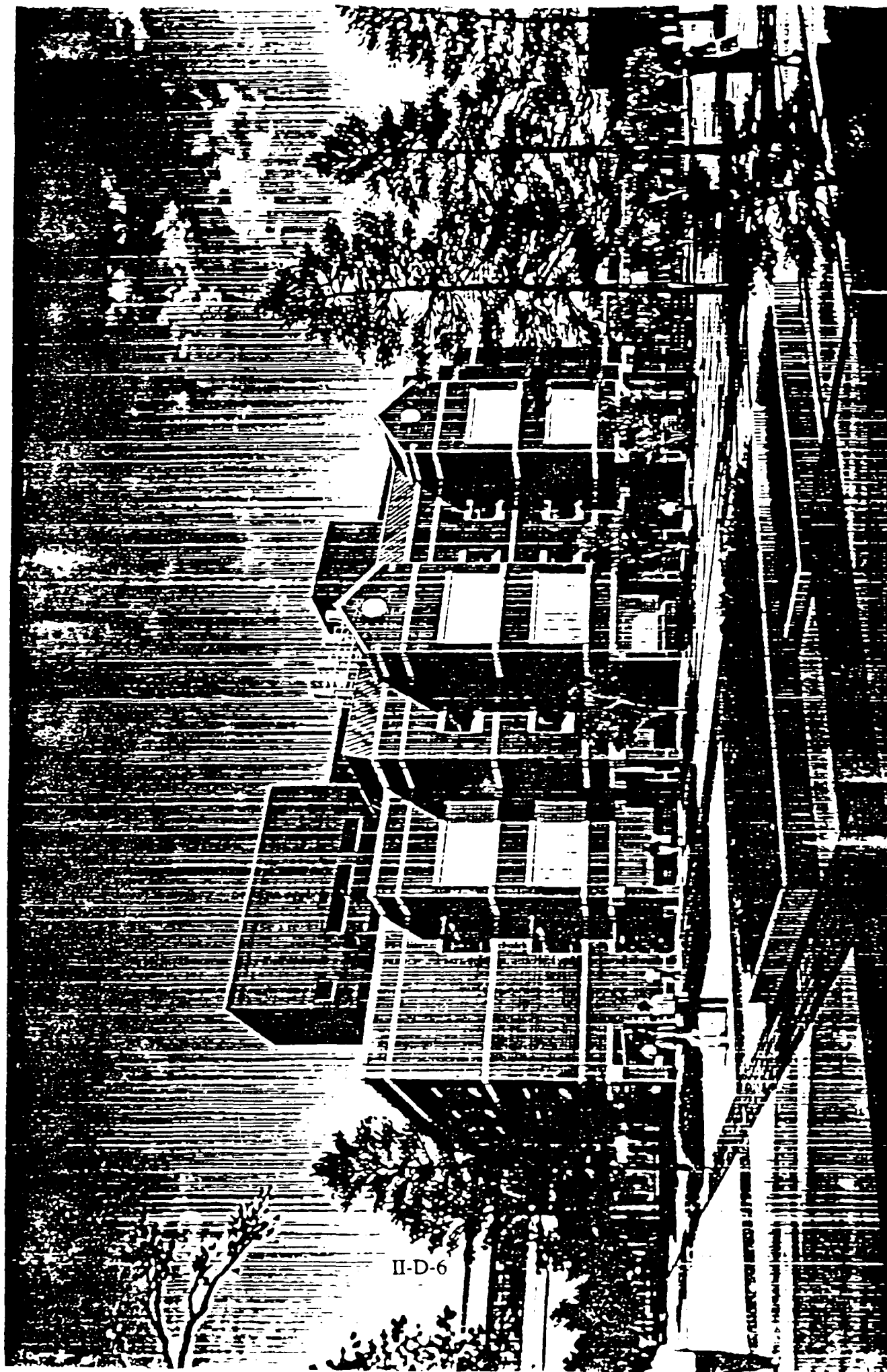
- ◆ Phase I – 55,000 sq. ft. (Ground breaking early Summer)

- ◆ Phase II – 110,000 sq. ft. (Future)

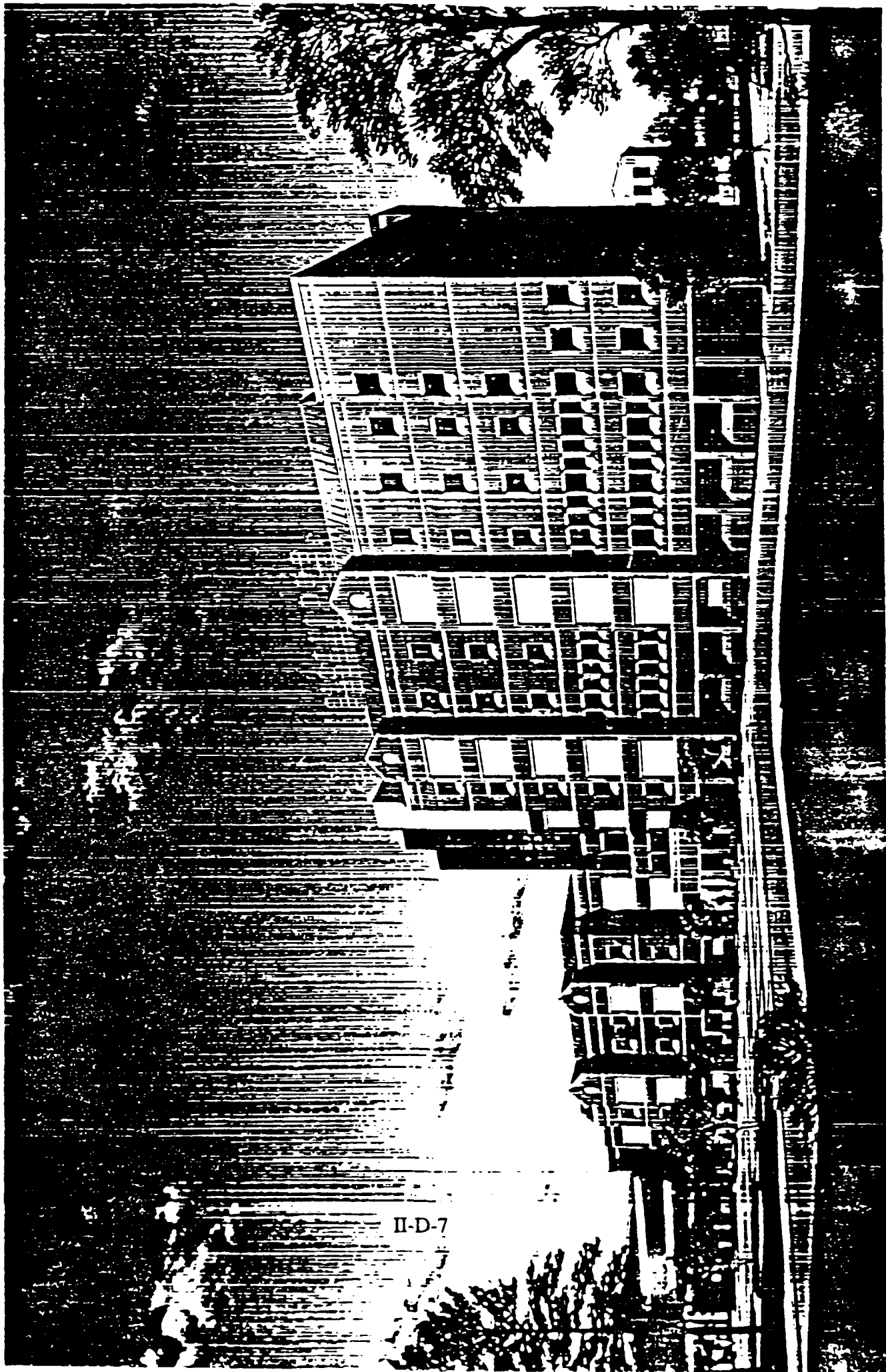
- Ph. D. Materials Science and Engineering

- ◆ Expanded to include Chemistry and Physics as well as Engineering

- ◆ New Chairman – Ronald Elsenbaumer – Polymer Chemist from Allied-Signal



II-D-6



II-D-7

September, 1986 – December, 1991

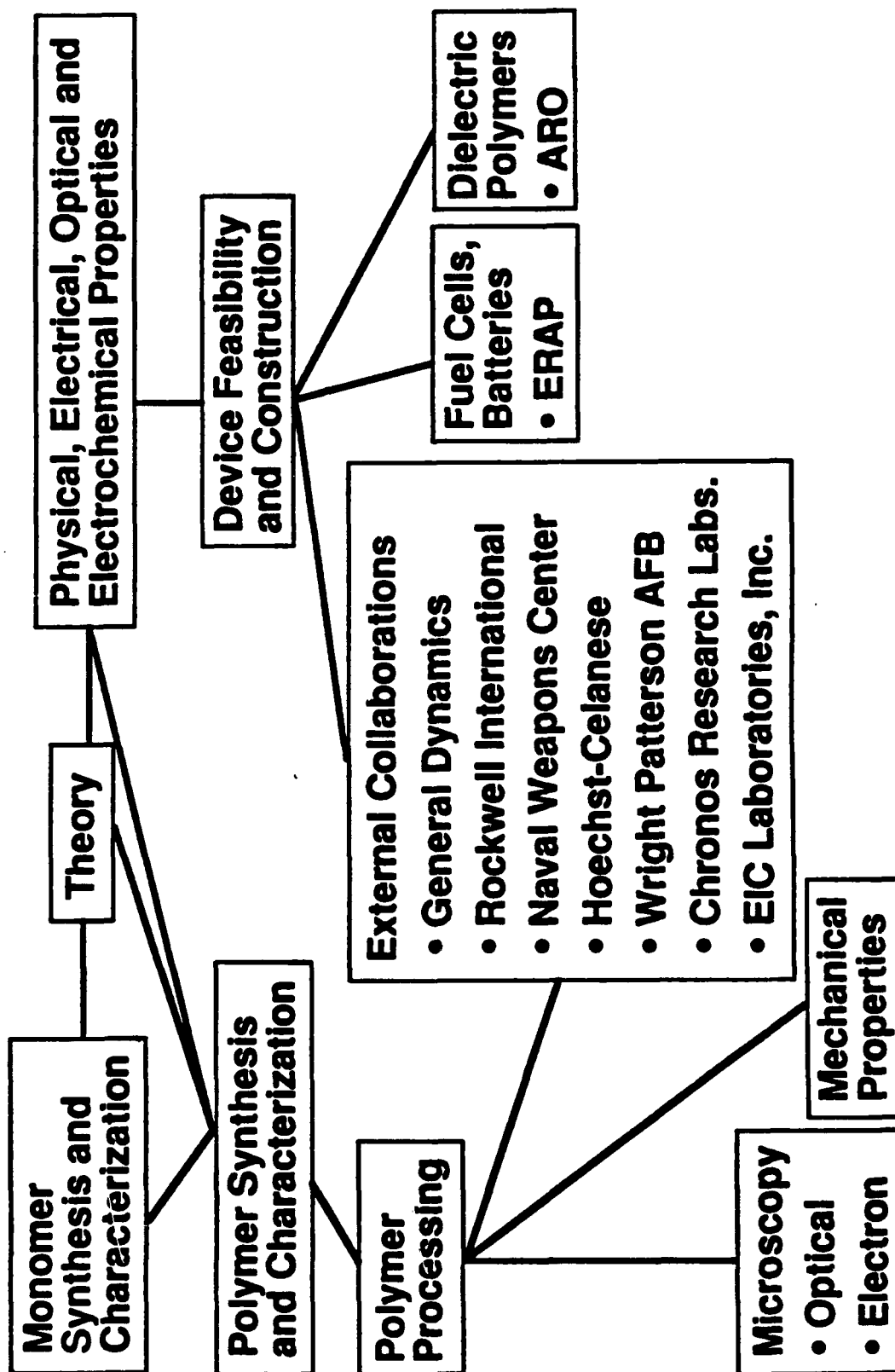
- **Statistical Summary – Publications**

- ◆ **80 Papers**
- ◆ **60 Presentations at Scientific Meetings**
- ◆ **1 Patent**

- **Statistical Summary – Personnel**

- ◆ **17 Graduate Students Supported**
- ◆ **21 Postdoctoral Associates Supported**
- ◆ **12 Undergraduates Supported**

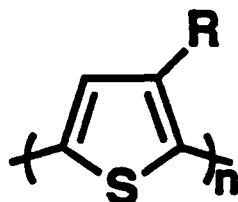
ELECTRONIC AND IONIC TRANSPORT IN
PROCESSABLE CONDUCTING POLYMERS
CENTER FOR ADVANCED POLYMER RESEARCH
THE UNIVERSITY OF TEXAS AT ARLINGTON



1986 - 1991 MAJOR RESEARCH ACCOMPLISHMENTS

- **Poly(3-alkylthiophene) Fibers**
- **Near IR Absorbing Metal Complex Polymers**
- **Batteries**
- **Theory**
- **Soluble Low Band-gap Polymers**
- **Isoregic Polyheterocycles**
- **In Situ Charge/Ion Transport Measurements**
- **Platinum/Polypyrrole Nanocomposites**
- **High Aspect Ratio Polyelectrolytes**
- **Aerospace Applications**

Poly(3-alkylthiophenes)



$R = C_4H_9, C_6H_{13}, \underline{C_8H_{17}}, \underline{C_{10}H_{21}}, C_{12}H_{25}$

Fibers and Films

Hoechst-Celanese

M. Ishaq Haider and Michael Jaffe

Electron Microscopy

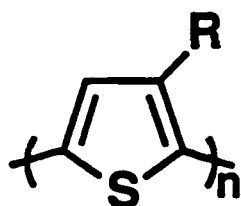
Howard J. Arnott and Linda Lopez

Center for Electron Microscopy

Department of Biology

University of Texas at Arlington

POLY(3-ALKYLTHIOPHENES) **GPC MOLECULAR WEIGHTS**

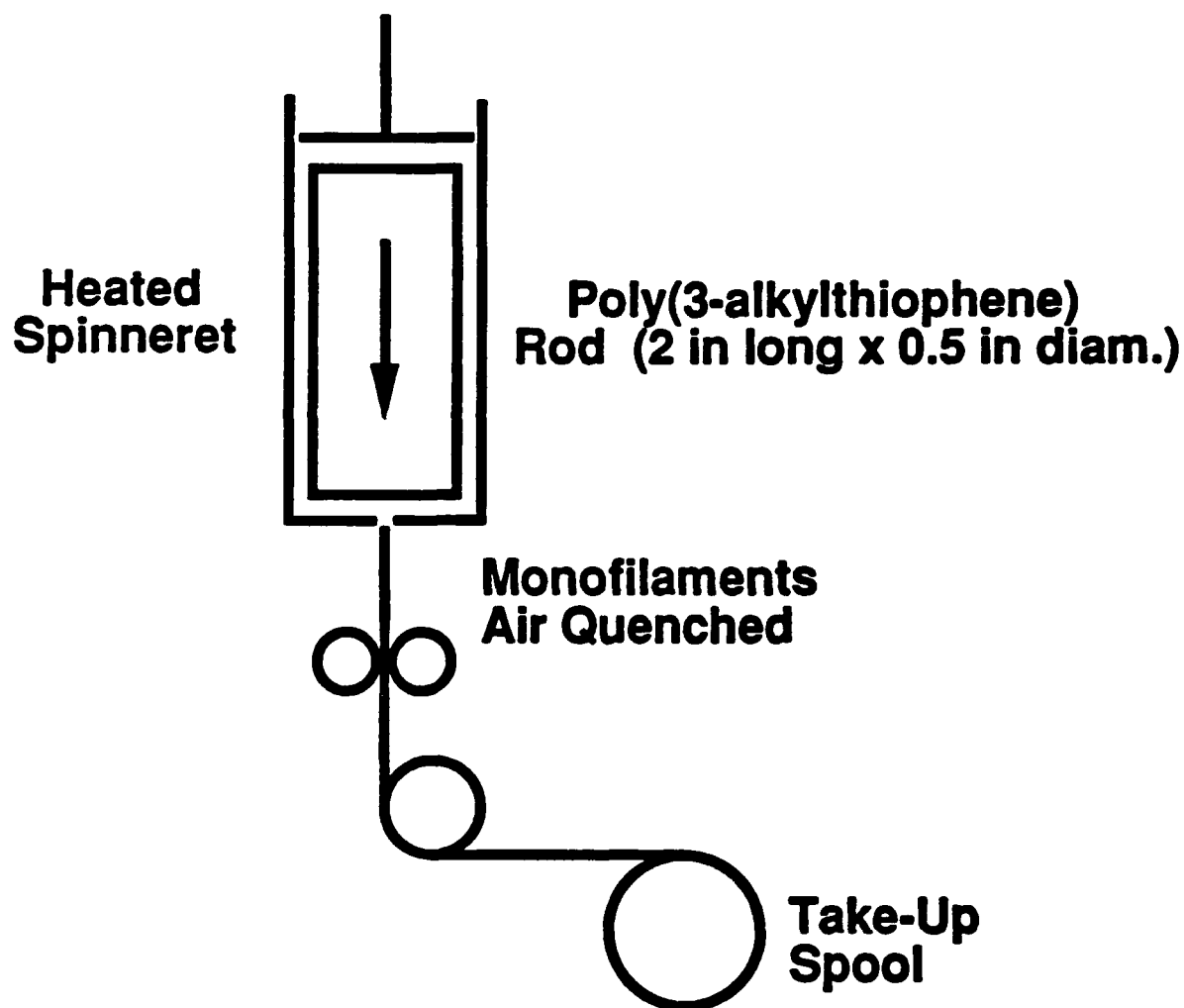


**{ Ultrastyrigel columns
 10,000, 500 and 100 Å }**

R	Multiangle Laser Light Scattering Detector (MALLS)			
	\bar{M}_w	\bar{M}_n	Peak Max.	\bar{M}_w/\bar{M}_n
C₄H₉	340,000	205,000	280,000	1.7
C₆H₁₃	398,000	297,000	320,000	1.3
C₈H₁₇	204,000	136,000	190,000	1.5
C₁₀H₂₁	390,000	187,000	260,000	2.1
C₁₂H₂₅	227,000	99,000	88,000	2.5

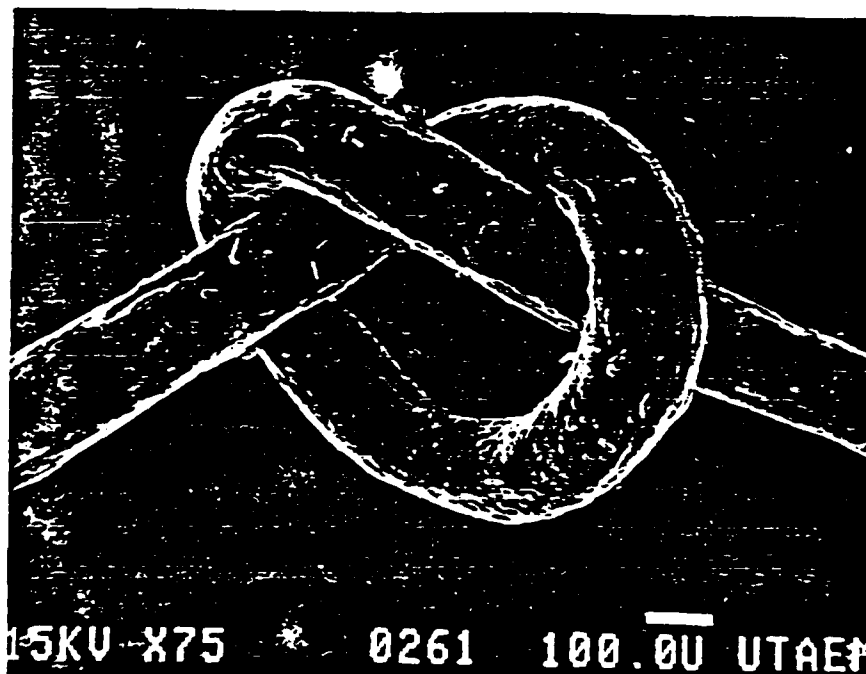
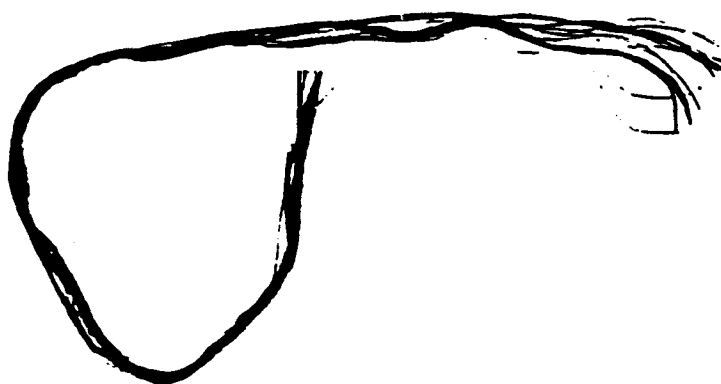
Melt-Spinning of Fibers

Collaboration with Hoechst-Celanese



MELT-SPUN FIBERS OF POLY(3-DECYLTHIOPHENE)

Montvale, N.J. 07645
MONTVALE N.J. 07645



**Melt-Spun Fiber of Poly(3-decylthiophene)
SEM Cross Section**

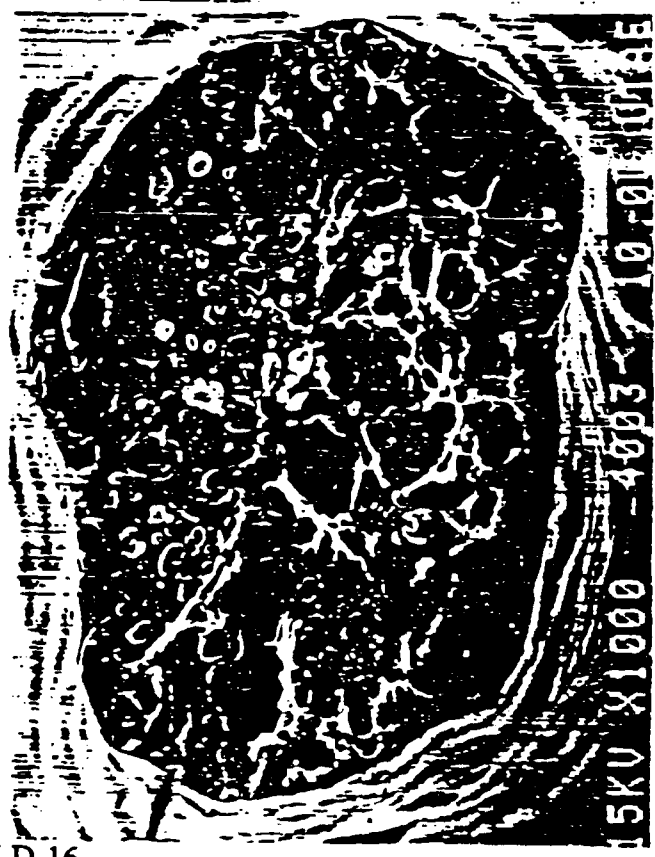


II-D-15

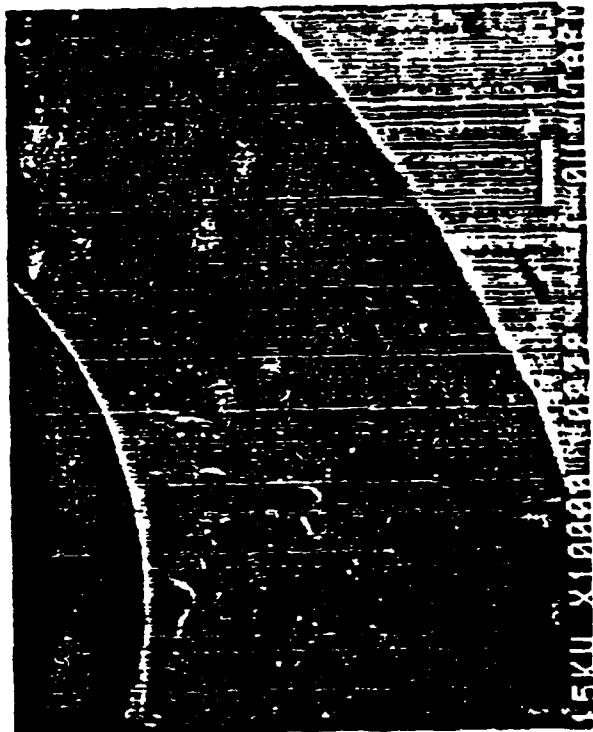
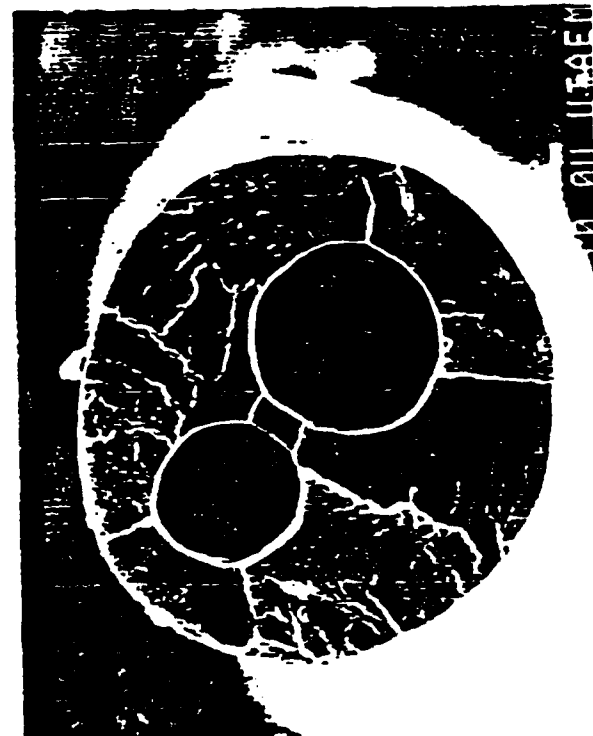
Handwritten notes:
(100x) 10-12-1960
poly 3-thiophene

**BLEND OF
40% POLY(3-DECYLTHIOPHENE) AND
60% LOW DENSITY POLYETHYLENE
MELT-SPUN FIBER
(HOECHST-CELANESE)**

II-D-16



FIBER OF BLEND OF 60% POLY(3-DECYLTHIOPHENE) AND 40% LOW DENSITY POLYETHYLENE FROM XYLENE SOLUTION



II-D-17

When heated
polymer
decomposes
into
gas & liquid
products

William O'Connell
Dundee

Conductivities – Doped with FeCl_3

Pure –

Poly(3-decylthiophene) fibers (melt-spun and solution pulled) and films (solution cast) 5 S cm⁻¹

Blends –

Phase separated 40%-poly(3-decylthiophene) and 60%-L. D. polyethylene fiber < 10⁻⁸ S cm⁻¹

60%-poly(3-decylthiophene) and 40%-L. D. polyethylene fiber 5 S cm⁻¹

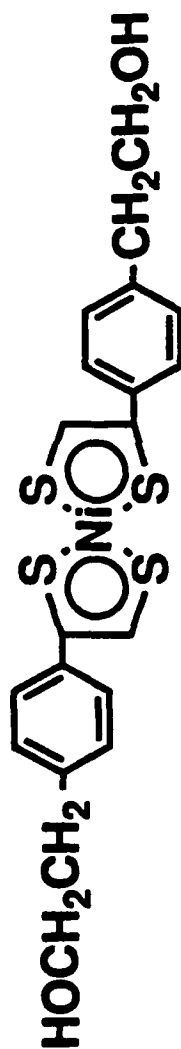
**60%-poly(3-decylthiophene) and 40%-L. D. polyethylene hot rolled film – parallel 6 S cm⁻¹
perpendicular 2 S cm⁻¹**

TRANSITION METAL COMPLEX POLYMERS

- **Charge Induction via Metal Ions as Opposed to Doping**
- **Conjugated Bridging and Flexible Connecting Ligands**
- **Solution Processable Homogeneous Polymers**
- **Intrinsically Conducting**
- **Electrochemically Active**
- **Non-linear Optical Properties**
- **Near Infrared Filtering Materials (Patent Pending)**

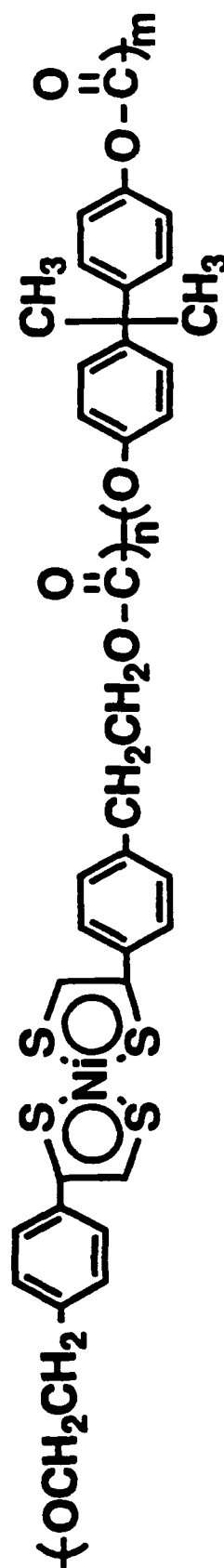
Near Infrared Absorbing Nickel bis(Dithiolene)

Complex Polymers



**Monomer
Synthesized in 6 steps**

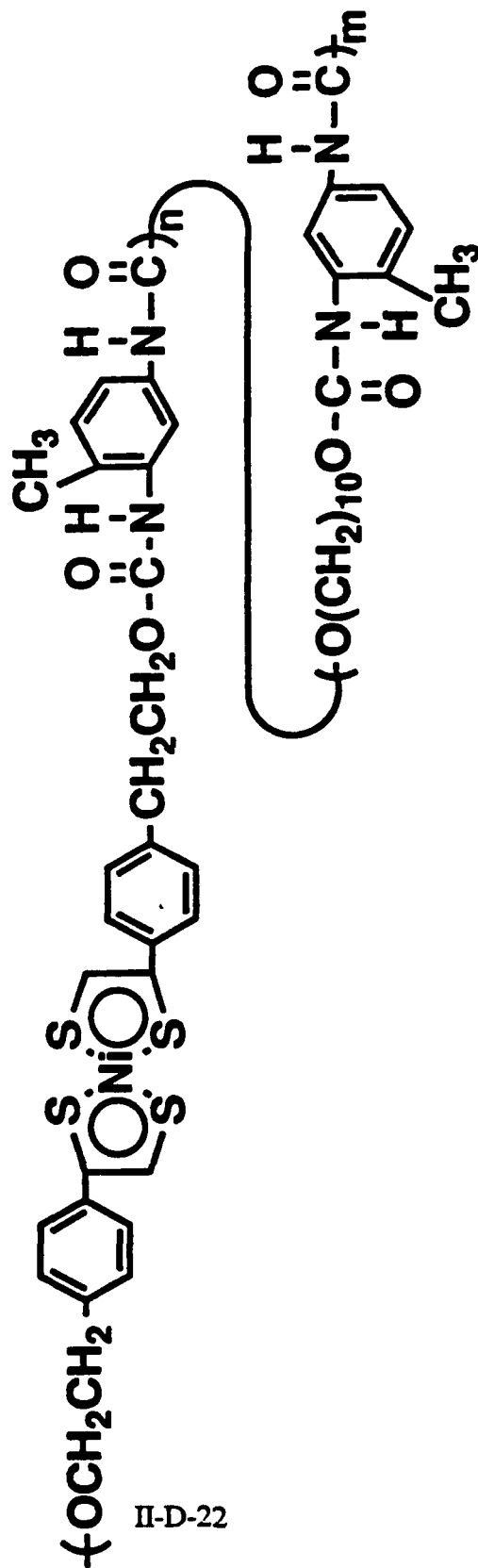
Polycarbonates (with bisphenol-A and phosgene)



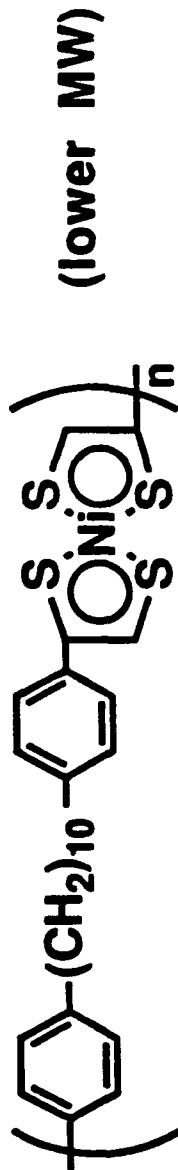
Long term stability & filters?

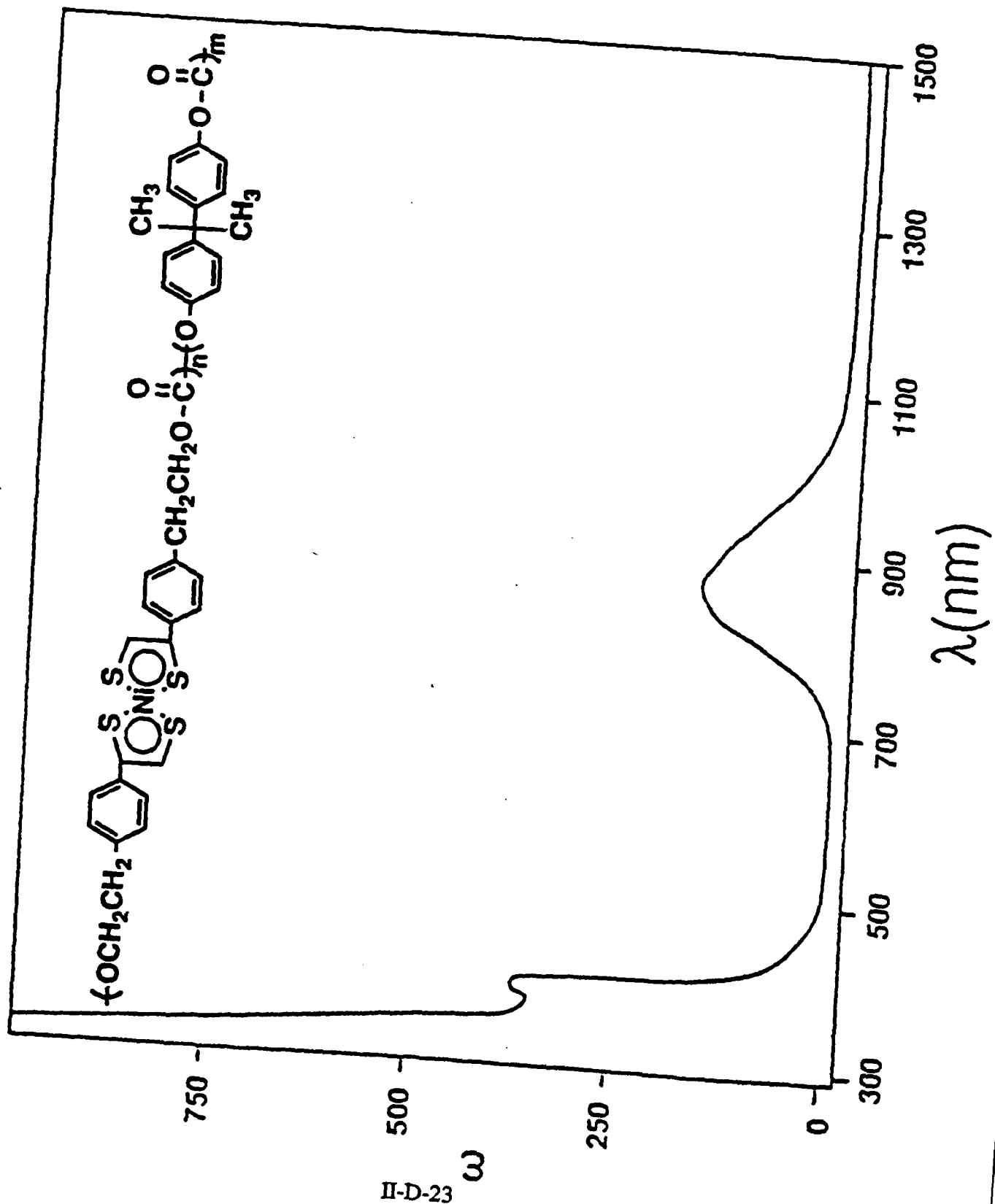
Near Infrared Absorbing Nickel bis(Dithiolene) Complex Polymers

Polyurethanes (with 1,10-decanediol and tolylene-2,4-diisocyanate)



"Decane linkage" polymer





Near Infrared Spectral Data of the
Nickel bis(Dithiolene) Complex Polymers

		Decane Linkage		Poly- carbonate		Poly- urethane	
		Dielectric					
Solvent	Constant	λ_{\max} (nm)	λ_{\max} (nm)	λ_{\max} (nm)	λ_{\max} (nm)	λ_{\max} (nm)	λ_{\max} (nm)
Toluene	2.4	847	840	840	840	840	840
CHCl ₃	4.8	—	845	845	830	830	830
THF	7.6	880	845	845	838	838	838
HMPA	30.0	927	930	930	930	930	930
DMF	36.7	935	932	932	933	933	933
DMSO	46.6	941	942	942	942	942	942

BATTERIES AND FUEL CELLS

DEVICE DEVELOPMENT

• Batteries

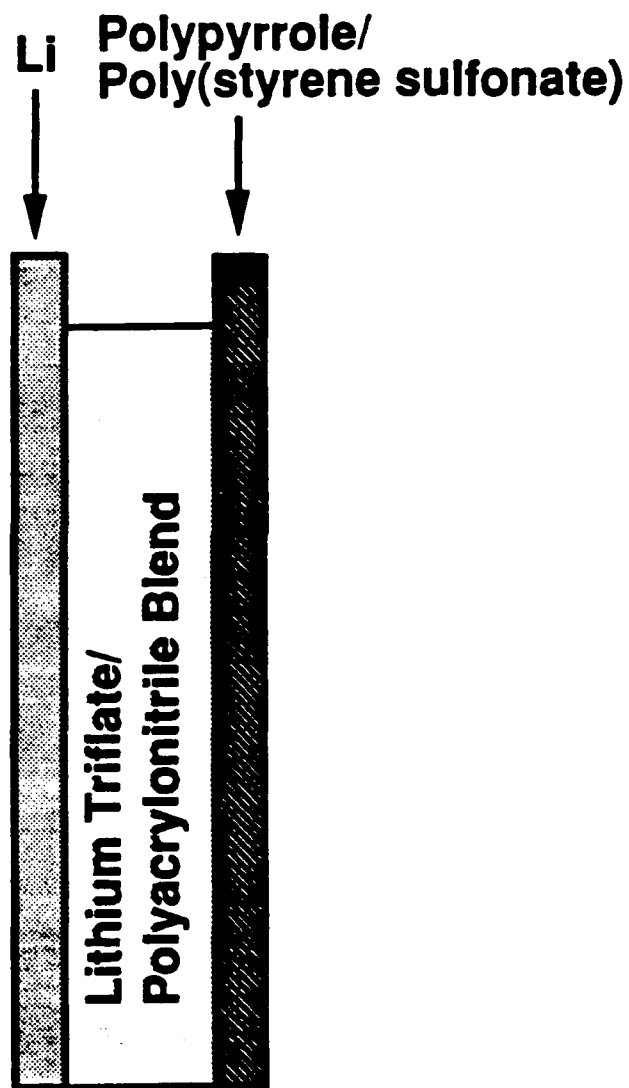
- ◆ Extensive testing done with polypyrrole in both aqueous solution and with solid polymer electrolytes
- ◆ Prototype batteries developed in collaboration with EIC Laboratories, Inc., Norwood, MA

II-D-25

• Fuel Cells

- ◆ New technology developed for electrode materials with unusual catalytic activity
- ◆ Considerable catalyst material savings demonstrated with new nanocomposite electrodes

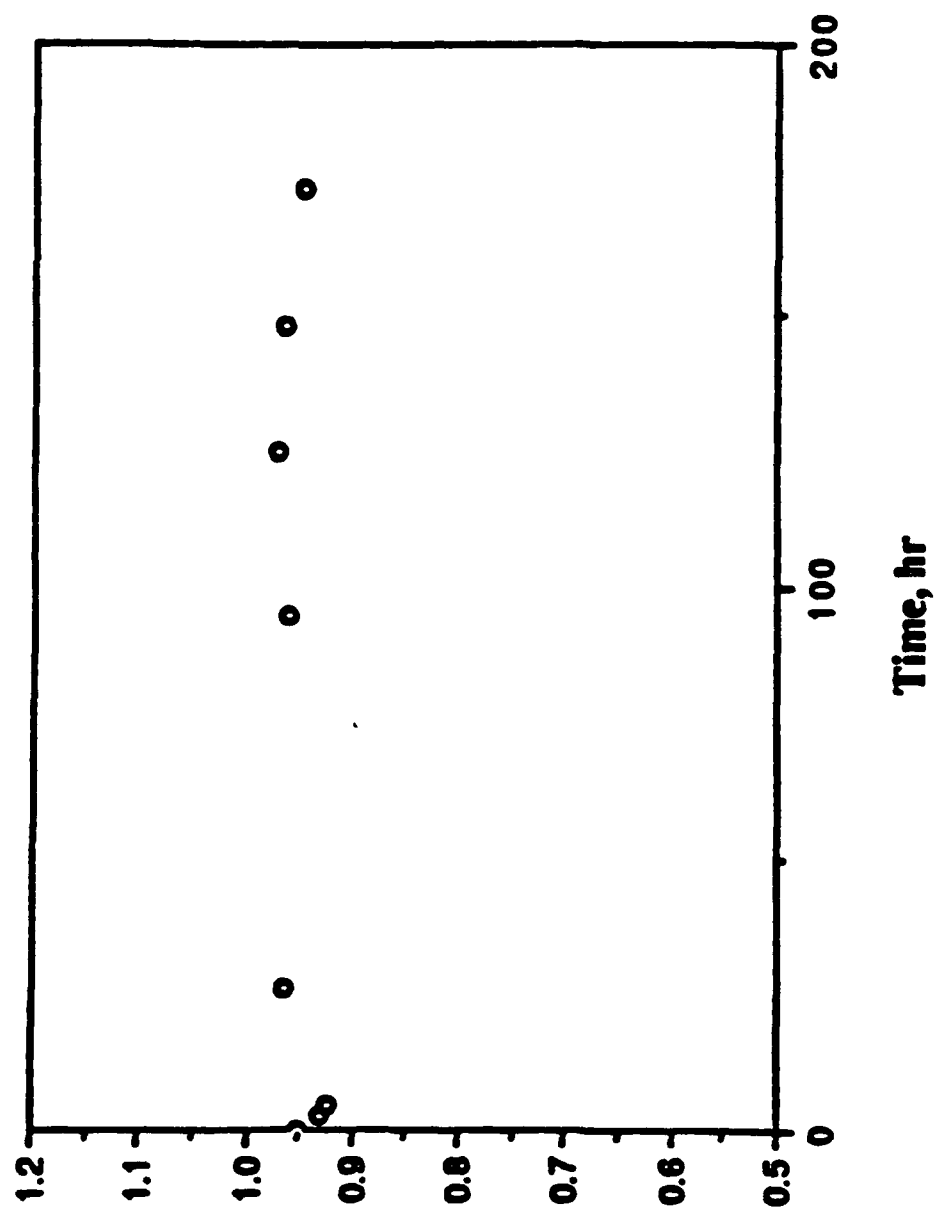
Prototype Battery



**Very Stable Charge-Discharge
Characteristics**

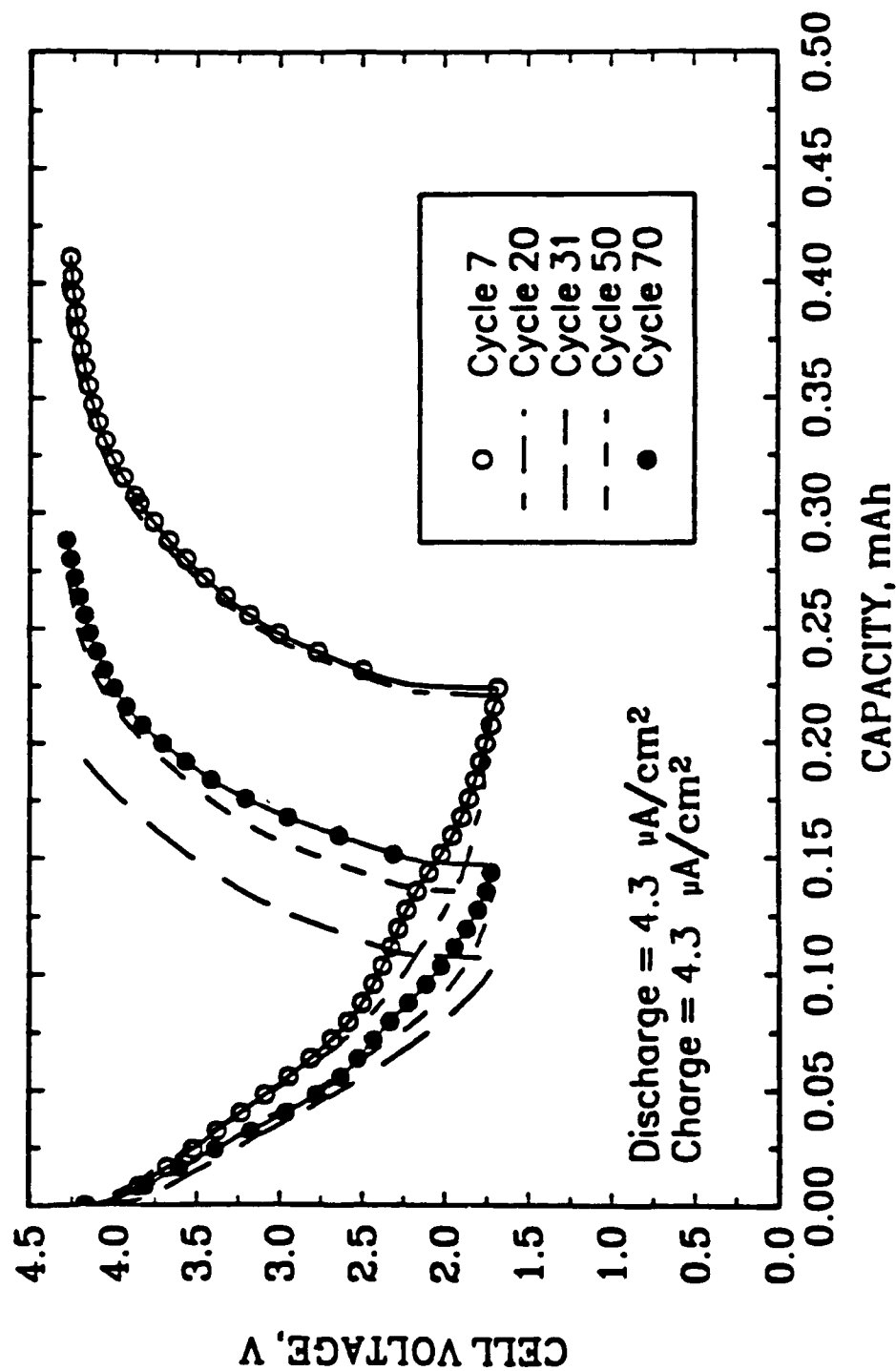
Zn electrode.

OCV Stability of Aqueous Polypyrrole Battery



OCV, Volt
II-D-27

Lithium/Polymer Electrolyte/Polypyrrole Cell Cell UT01, Substrate= Carbon Paper



Just
Power

2009/10

WHY POLYHETEROCYCLES?

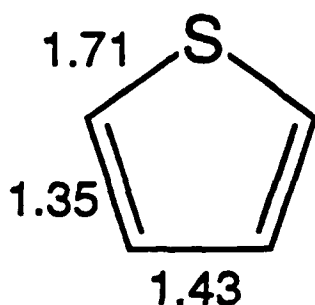
- Broad property variations tunable via molecular structure
 - conductivity (10^{-15} - $10^{+3} \Omega^{-1} \text{ cm}^{-1}$)
 - color (full spectral range including transparent)
 - ion transport (selective ion supply)
- Easily prepared using common chemical and electrochemical methods.
- Broad variety of dopant ion systems applicable
 - monoanionic and multianionic small molecules to polyelectrolytes
- Melt and solution processable
 - films
 - fibers
 - coatings
- Easily switchable between conducting and insulating states

- **Stable as conductors and insulators**
 - **high thermooxidative stability**
 - **long-term stability**
 - **stable in electrolytes**
- **Multi-component materials**
 - **polymer-polymer blends**
 - **molecular composites**
 - **laminates**
- **Controllable surface chemistry**
 - **adhesion**
 - **biocompatible**

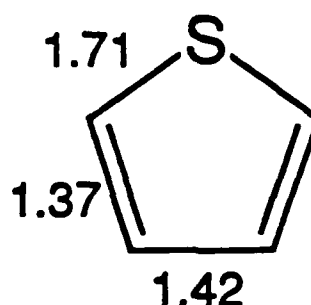
THEORETICAL DESIGN

Goal: To develop molecular orbital calculation methods, and use available theoretical techniques, to guide experimentalists in the synthesis of conducting polyheterocycles with controllable optoelectronic properties.

Molecular → Oligomer → Polymer Geometries



C-S-C = 93°
S-C-C = 112°
C-C-C = 112°



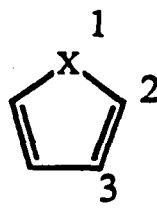
C-S-C = 92°
S-C-C = 112°
C-C-C = 113°

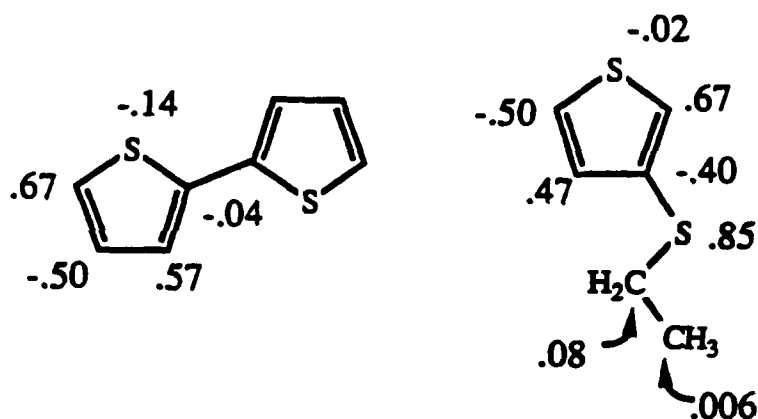
Band Theory (Modified Extended Hückel)

- substituent effects
- polymer conformation effects

Radical-Cation Spin Densities

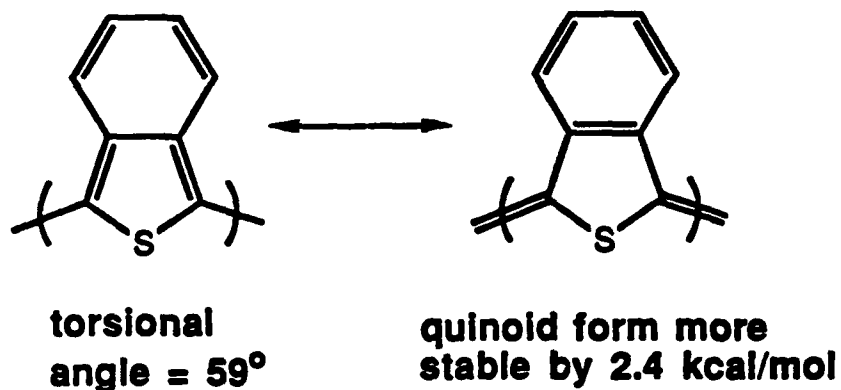
- oxidatively activated step-growth polymerization
- theory specifies site for polymerization and suggests potential defects (branches or crosslinks)
- electrochemical film formation requires conjugated conducting polymer

	X	Spin Density at Position		
		1	2	3
	S	-.20	.67	-.01
	O	-.15	.66	-.03
	NH	-.27	.69	.00
	PH	.97	-.15	.54

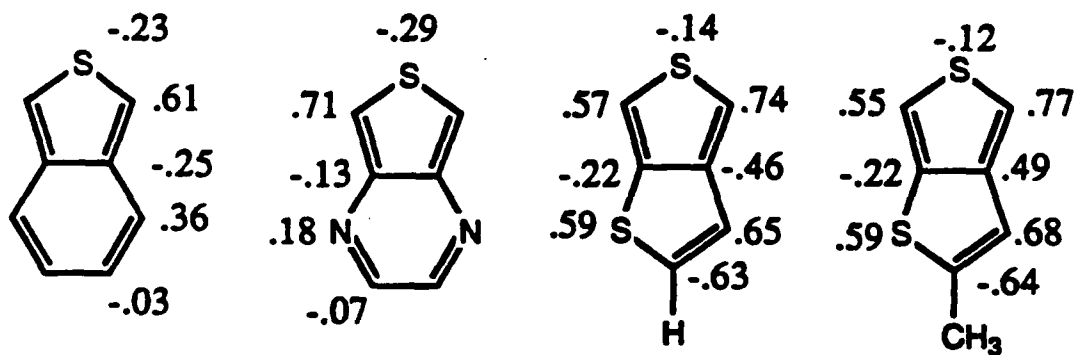


Low Band-Gap "Transparent" Conducting Polymers

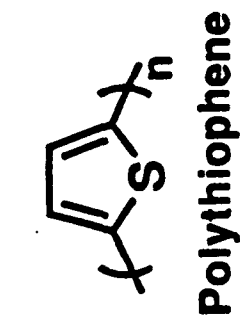
- reduce bond length alternation



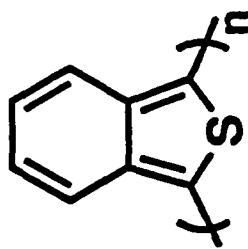
Spin Density Calculations



LOW BAND-GAP, "TRANSPARENT" CONDUCTING POLYMERS

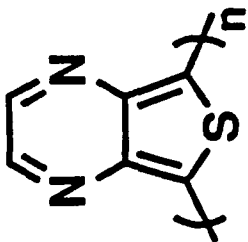


PT



Poly(isothianaphthene)

PITN



Poly(thieno[3,4-b]pyrazine)

PTHP

Band Gaps

	Extended Hückel (eV)	Experimental (eV)
PT(arom/planar)	1.76	2.0-2.2
PITN(arom/planar)	0.68	1.0 (1.0-1.3)
(arom/non-planar)	1.64	1.0 (1.0-1.3)
(quinoid)	0.80	1.0 (1.0-1.3)
PTHP(arom/planar)	0.12	[1.1 (soln)]
(quinoid)	0.70	[1.1 (soln)]

Nayak, K.; Marynick, D. S. *Macromolecules* 1990, 23, 2237.

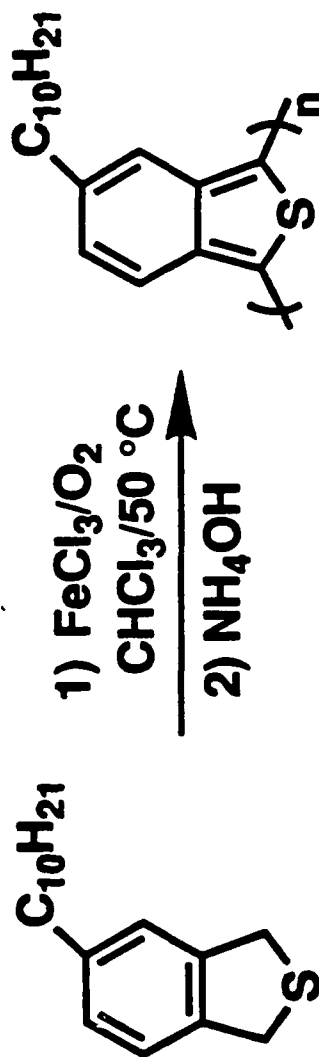
Spindler
Low band gap
transparent
conducting
polymers

band gap (eV)
calculated
values

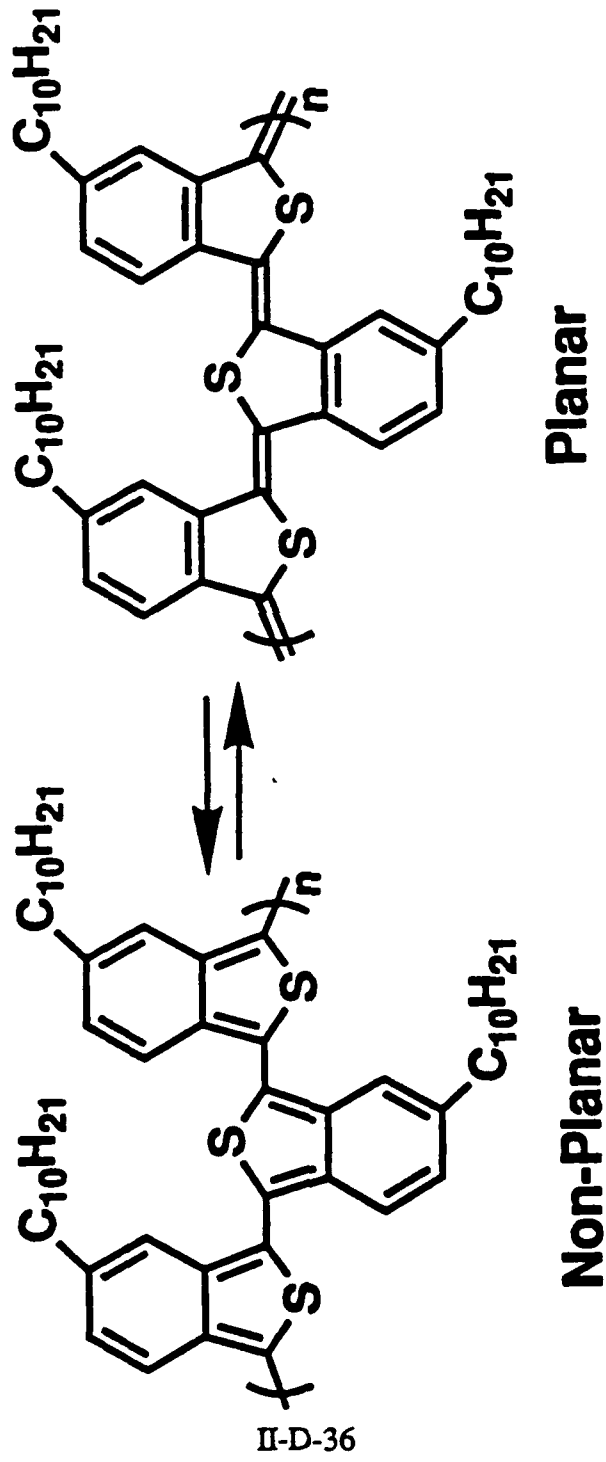
LOW BAND-GAP, "TRANSPARENT"
CONDUCTING POLYMERS

POLY(5-DECYLBENZO[c]THIOPHENE)
[POLY(5-DECYLISOTHIANAPHTHENE)]

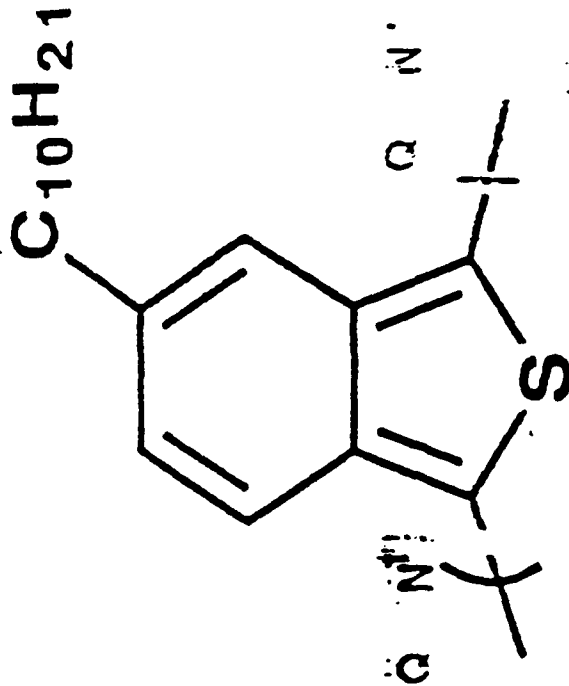
II-D-35



**POLY(5-DECYLBENZO[c]THIOPHENE)
[POLY(5-DECYLISOTHIANAPHTHENE)]**



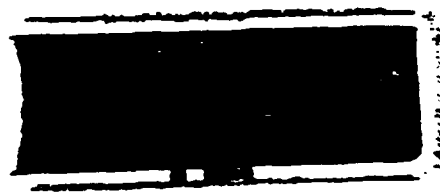
II-D-36



DOPED WITH
 $NO^+BF_4^-$

U/A

↑
Correct

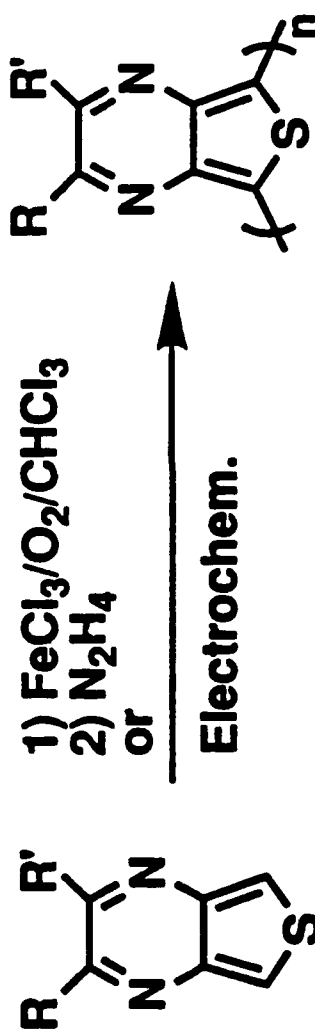


UNDOPED

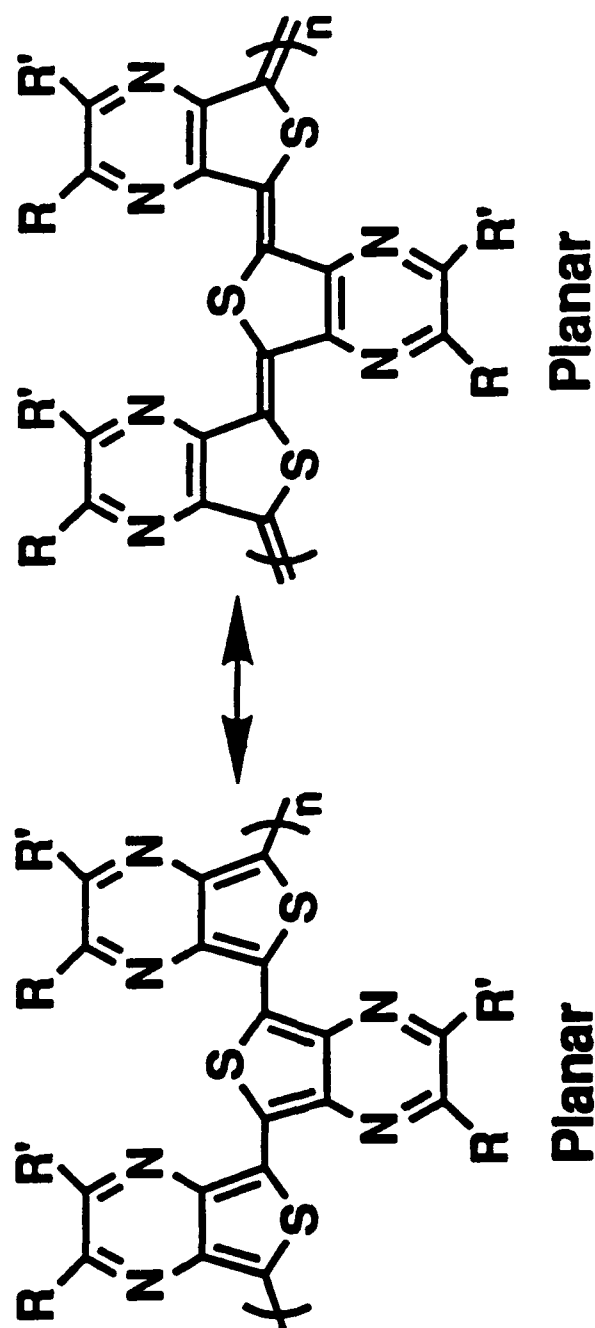
II-D-37

LOW BAND-GAP, "TRANSPARENT"
CONDUCTING POLYMERS

POLY(2,3-DIALKYLTHIENO[3,4-b]PYRAZINE)

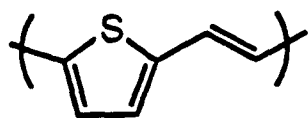


POLY(2,3-DIALKYLTHIENO[3,4-b]PYRAZINE)



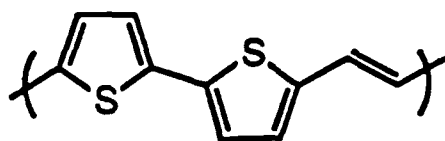
$$\Delta E = -4.2 \text{ kcal/mol}$$

Low Band-Gap Substituted Polyheterocycles



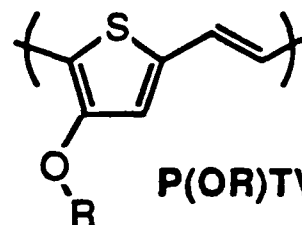
PTV ¹

$E_g = 1.75 \text{ eV}$



PDTE ²

$E_g = 1.8 \text{ eV}$

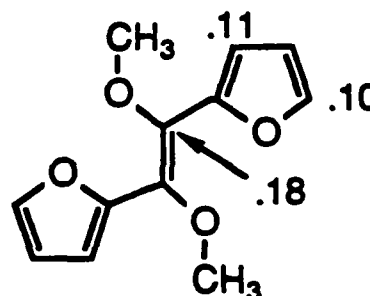
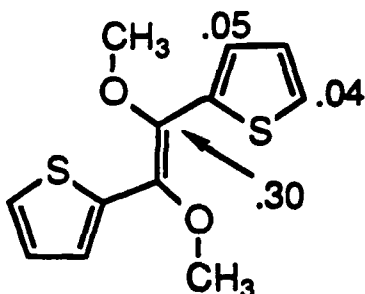


P(OR)TV ³

$E_g = 1.5 \text{ eV}$

MOLECULAR ORBITAL CALCULATIONS

- a guide to what NOT to do !



- both molecules are easily oxidized to form radical-cations
- maximum spin density on vinylene unit
- neither polymerize to form conducting polymer films

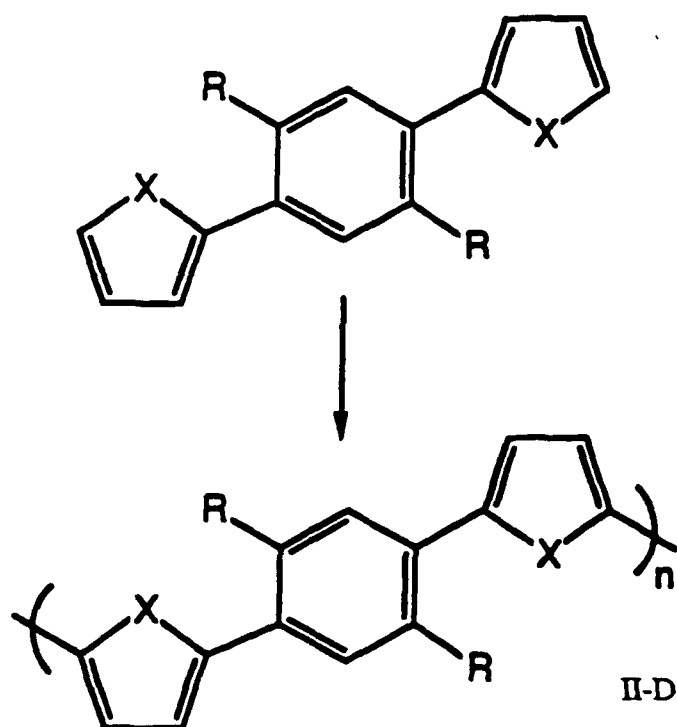
not polymerize

1. Jen, K.Y.; Maxfield, M.; Shacklette, L.W.; Elsenbaumer, R.L. *J. Chem. Soc., Chem. Commun.* 1987, 309.
2. Martinez, M.; Reynolds, J.R.; Basak, S.; Black, D.A.; Marynick, D.S.; Pomerantz, M. *J. Polym. Sci., Polym. Phys. Ed.* 1988, 26, 911.
3. Jen, K.Y.; Eckhardt, H.; Jow, T.R.; Shacklette, L.W.; Elsenbaumer, R.L. *J. Chem. Soc., Chem. Commun.* 1988, 215.

ISOREGIC POLYHETEROCYCLES

Bis(2-heterocycle)-*p*-phenylene Polymers

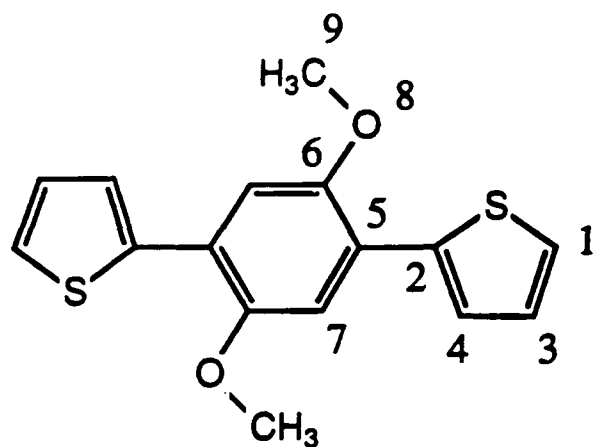
- Symmetric monomers yield no head-head coupling
- Ordered polymer systems
- Substituents on phenylene ring, facile chemistry, multiple derivatives
- Optical and electrochemical properties equivalent to or better than polyheterocycles
- Planar substituted conjugated polymers



$X = S, O, NH$

$R = H, -CH_3, -C_6H_{13},$
 $-OCH_3, -OC_7H_{15},$
 $-OC_{12}H_{25}, -OC_{16}H_{33},$
 $-OC_{20}H_{41}$

Radical-Cation Spin Densities



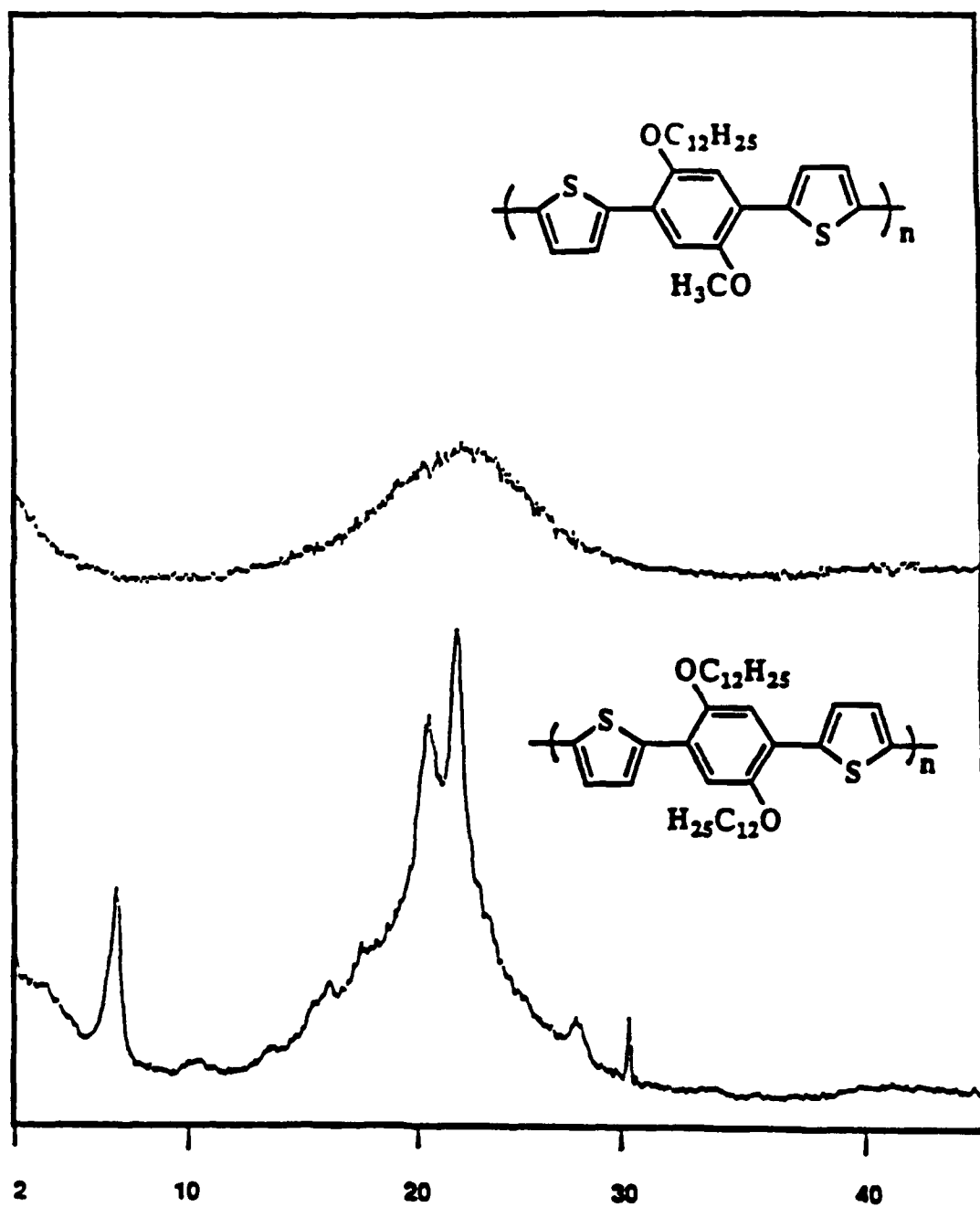
Site	Spin Density	
1	+0.69	←
2	-0.48	
3	-0.59	
4	+0.63	←
5	+0.35	←
6	+0.23	←
7	-0.32	
8	+0.08	
9	-0.03	

Molecular Conformations

heterocycle	substituents	torsional angle	barrier to planarity (kcal/mol)
-----	-----	-----	-----
thiophene	H/H	24°	3.1
thiophene	-OCH ₃ /-OCH ₃	40°	3.5
thiophene	-CH ₃ /-CH ₃	63°	15.8
furan	H/H	0°	0.0
furan	-OCH ₃ /-OCH ₃	0°	0.0
furan	-CH ₃ /-CH ₃	30°	0.5

Aregic and Isoregic Poly[1,4-bis(2-thienyl)phenylenes] X-ray Diffraction

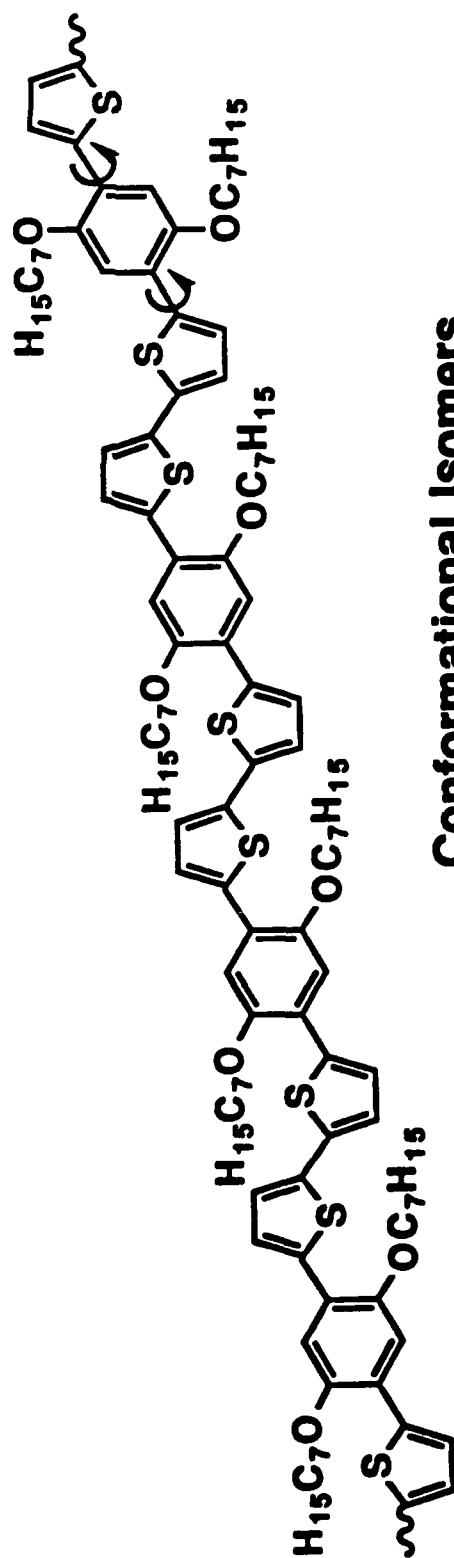
Intensity (Arbitrary Units)



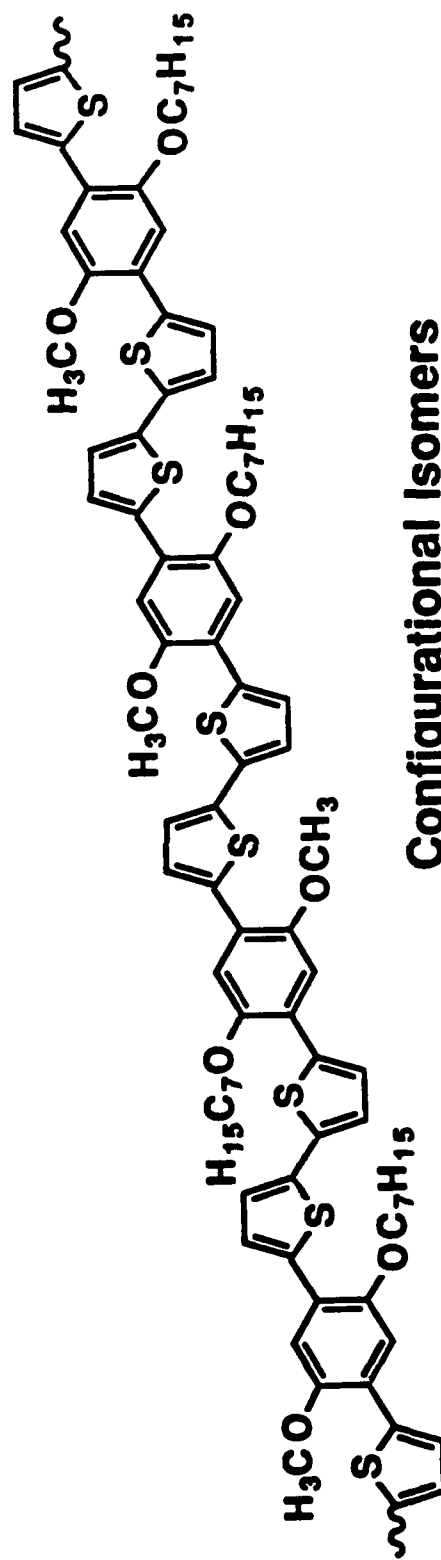
2θ (Degrees)

II-D-43

Isoregic vs. Aregic Poly[1,4-bis(2-thienyl)-2,5-dialkoxyphenylenes]



Conformational Isomers



Configurational Isomers

main stuff

ELECTRICAL CONDUCTIVITIES FOR DOPED POLY[1,4-BIS(2-HETEROCYCLE)-2,5-DISUBSTITUTED PHENYLENES]

HETEROCYCLE	SUBSTITUENTS	ELECTRICAL CONDUCTIVITY ($\Omega^{-1} \text{ cm}^{-1}$)	
Thiophene	H/H	5×10^{-1}	Pressed Pellets
Thiophene	CH ₃ /CH ₃ — <i>non-planar</i>	2×10^{-6}	
Thiophene	-OCH ₃ /-OCH ₃	2×10^0	
Thiophene	-OC ₇ H ₁₅ /-OC ₇ H ₁₅	1×10^0	Free Standing
Thiophene	-OC ₁₂ H ₂₅ /-OC ₁₂ H ₂₅	4×10^0	
Thiophene	-OC ₁₆ H ₃₃ /-OC ₁₆ H ₃₃	3×10^0	
Thiophene	-OC ₂₀ H ₄₁ /-OC ₂₀ H ₄₁	1×10^0	Cast Films
Thiophene	-OCH ₃ /-OC ₇ H ₁₅	2×10^{-1}	
Thiophene	-OCH ₃ /-OC ₁₂ H ₂₅	2×10^{-1}	
Thiophene	-C ₆ H ₁₃ /-C ₆ H ₁₃	3×10^{-8}	
Furan	H/H	2×10^{-1}	Electrochemically Synthesized Films
Furan	-CH ₃ /CH ₃	1×10^{-1}	
Furan	-OCH ₃ /-OCH ₃	4×10^{-1}	
Furan	-OCH ₃ /-OC ₇ H ₁₅	3×10^{-1}	
Furan	-OC ₇ H ₁₅ /-OC ₇ H ₁₅ II-D-45	4×10^{-1}	

*no substituent effect.
from 2-44-77*

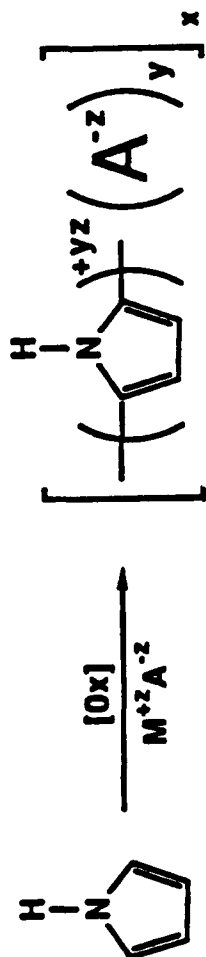
ELECTROCHEMICAL POLYMERIZATIONS

- Stable and electrically conducting films
- Free-standing and electrode supported
- Controllable Ion Transport
- Surface reactivity to proteins

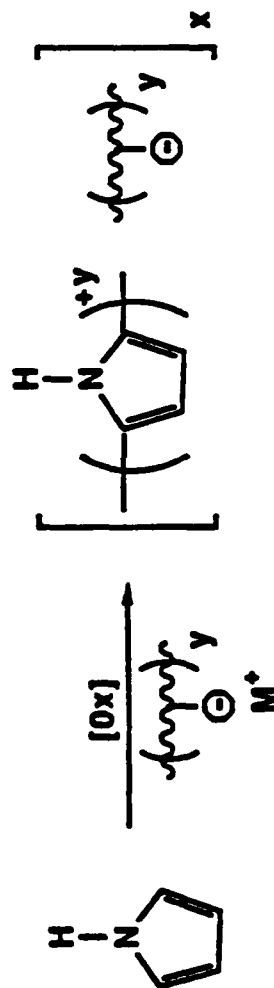
1602.1

*change
dopants.*

Monoanionic and Multianionic Dopant Ions



Polyelectrolyte Dopant Systems



IN-SITU PROBES OF REDOX SWITCHING

EPR Spectroscopy

- spins
- probes conjugated chain directly

UV-Vis-NIR Spectroscopy

- polarons/bipolarons
- active dopant ions
- in-situ derivatization (local pH measurements)

Luminescence

- active dopant ions (electrochemically silent)
- both anion and cation dominated transport

Electrochemical Quartz Crystal Microbalance

- mass change at electrode surface

Raman Spectroscopy

- probes polymer backbone structural changes

Electroactive Polymer Coatings in Solution

The Quartz Crystal Microbalance

In-Situ Solution Mass Changes

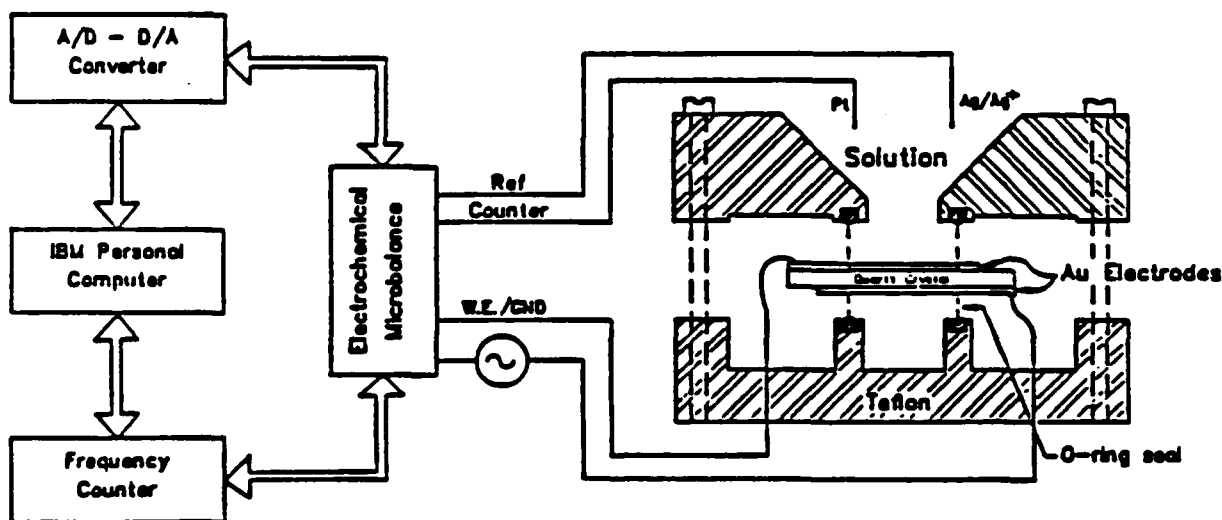
Ion and Redox Reagent Sensitive Polymers

Polymer Film Deposition Monitor

-Electrochemical Polymerization

Mechanism of Electrode Charge/Discharge

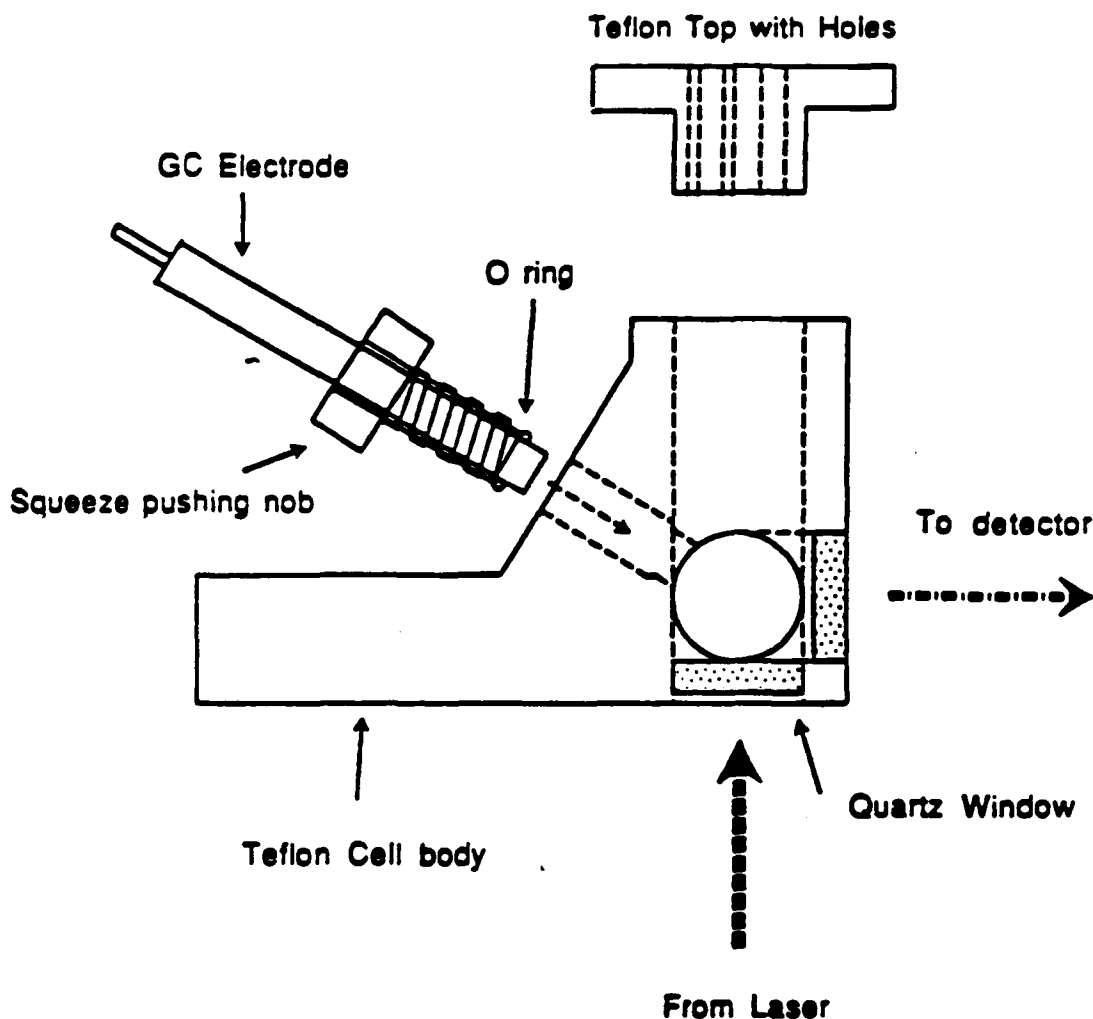
-Ionic Mobility



Applications

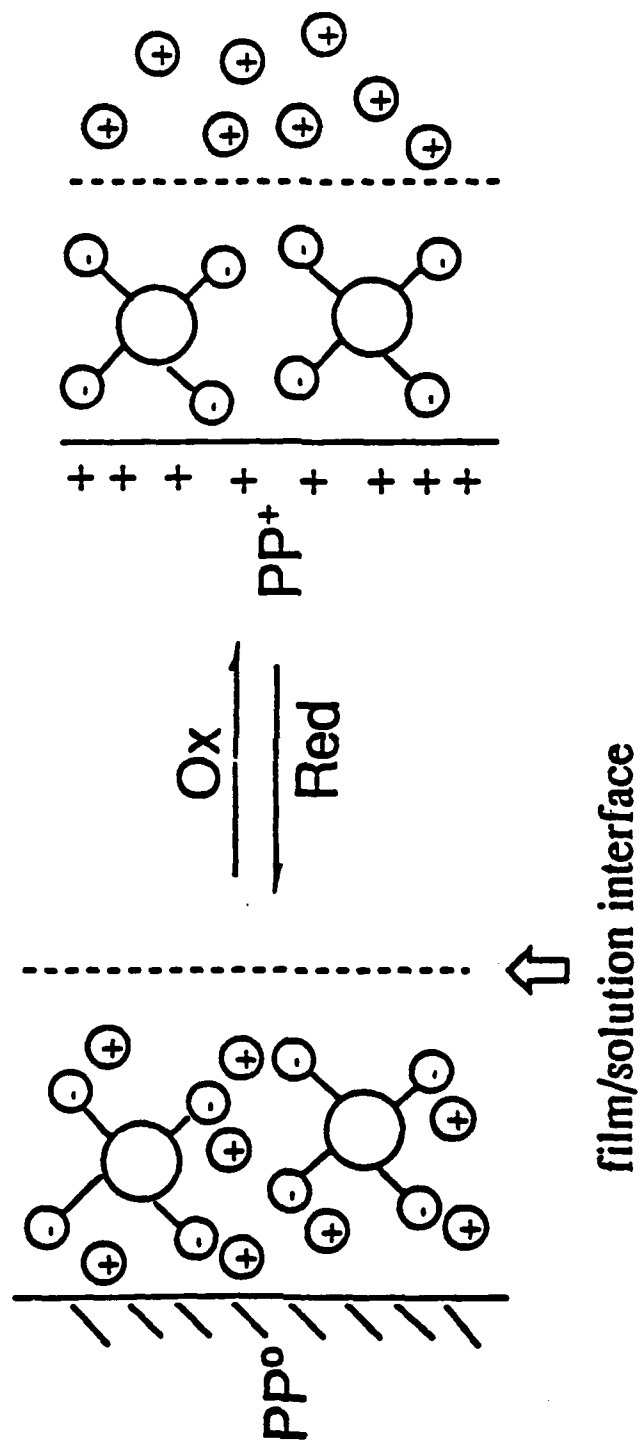
-Solution Phase Chemical and Biosensors

Potential Modulated Raman Spectroscopy

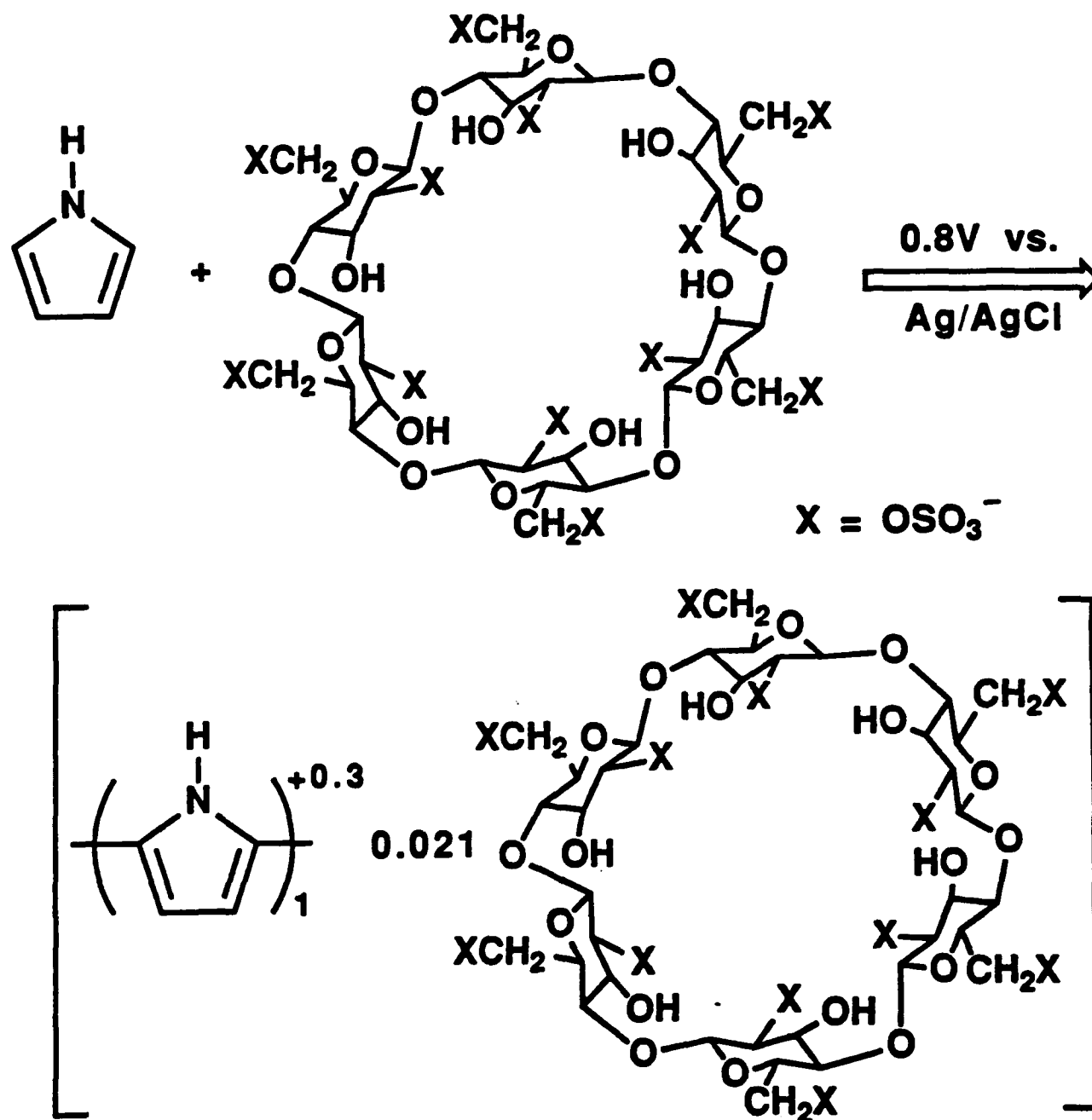


- probes backbone structural changes directly
- facile measurements in aqueous electrolytes (compare with FTIR)
- combination with voltammetry (CV-Raman) yields electrode potential dependence

Ion movement in polypyrrole doped with multianionic dopants

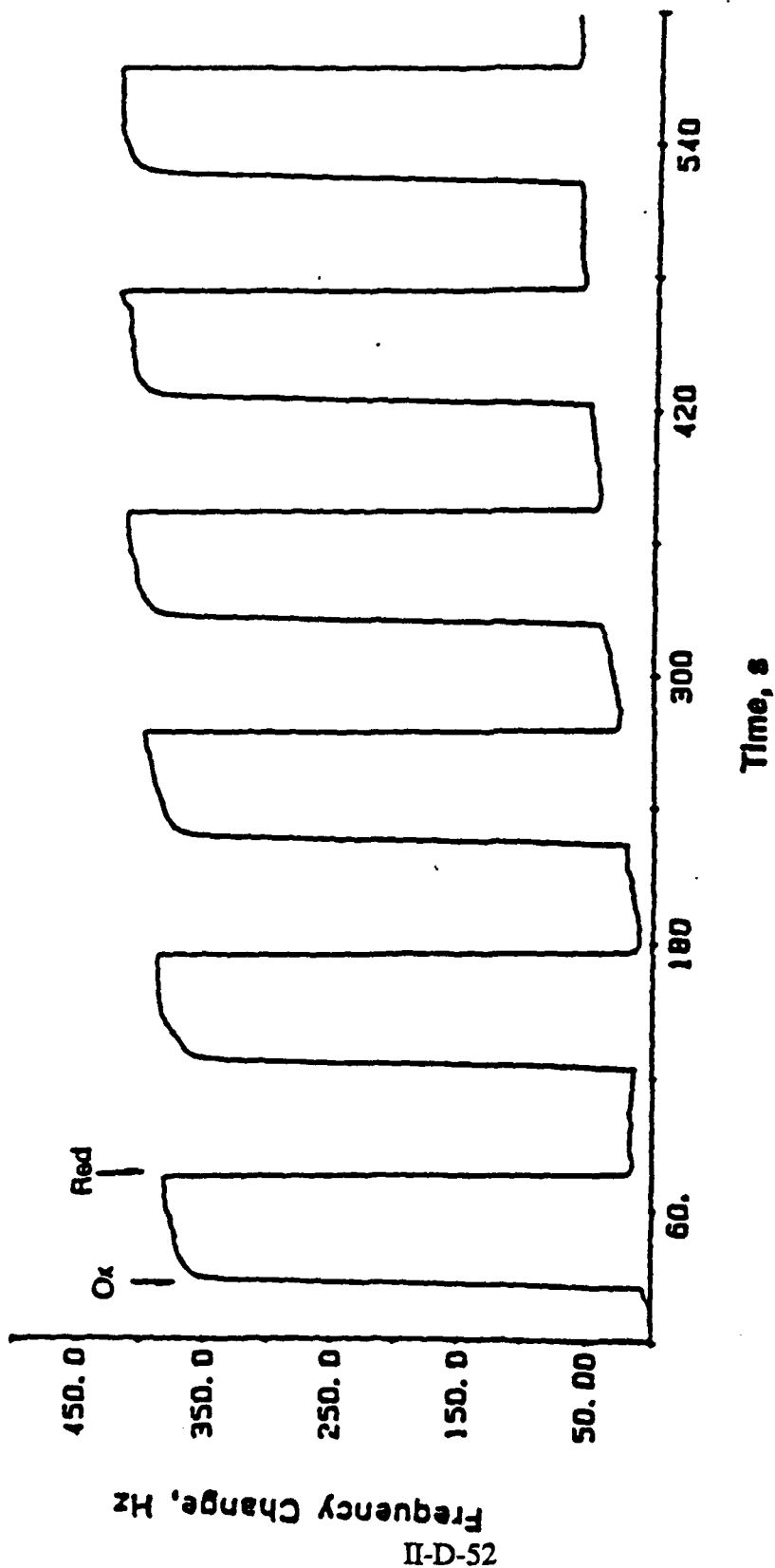


Electrosynthesis of Poly(pyrrole cyclodextrin tetradecasulfate)



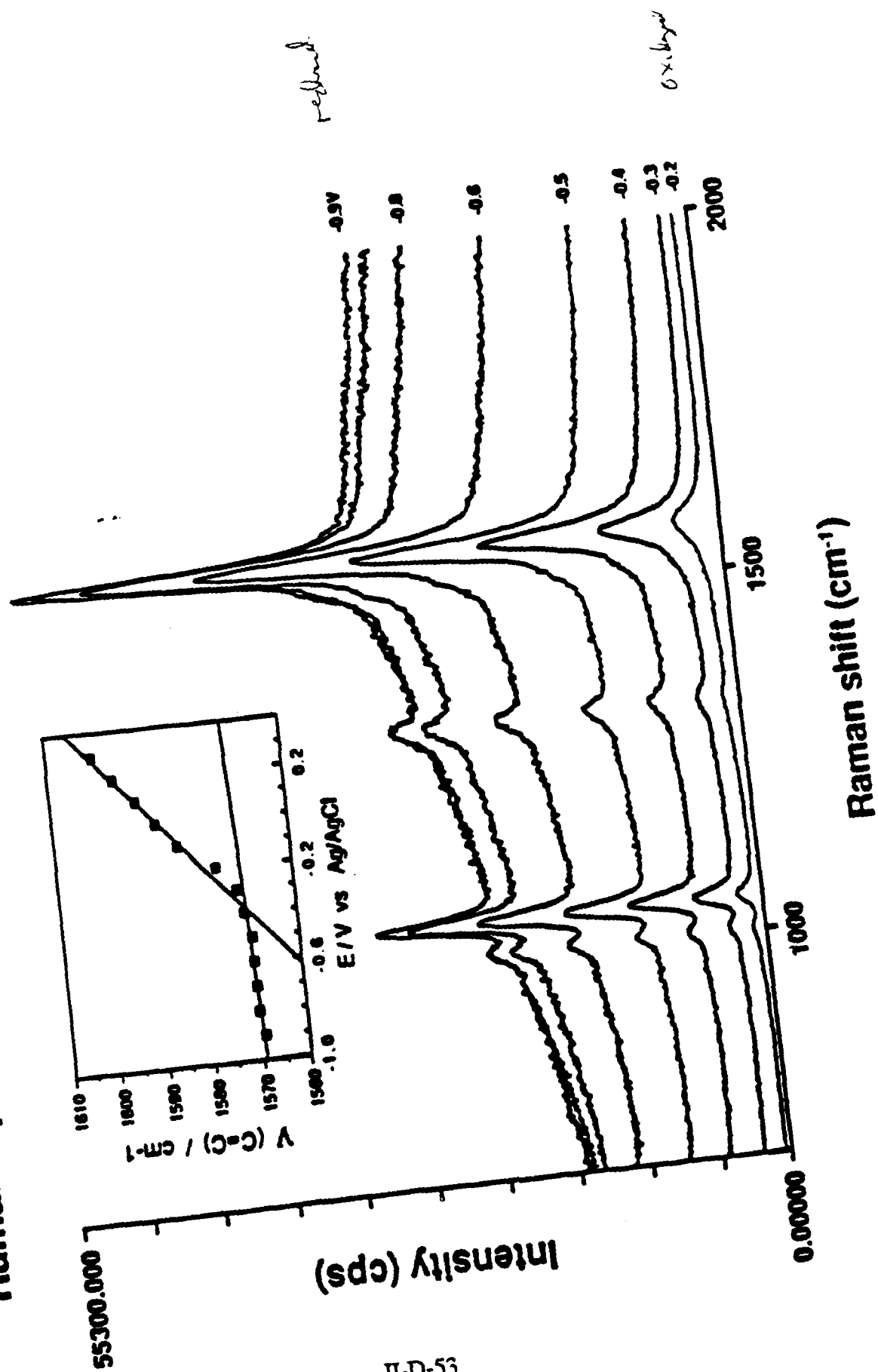
- PP-CDS is a black, electronically conducting film

OX - Oxidation from polymer film over Cs with $\sim 10^{-5}$ V

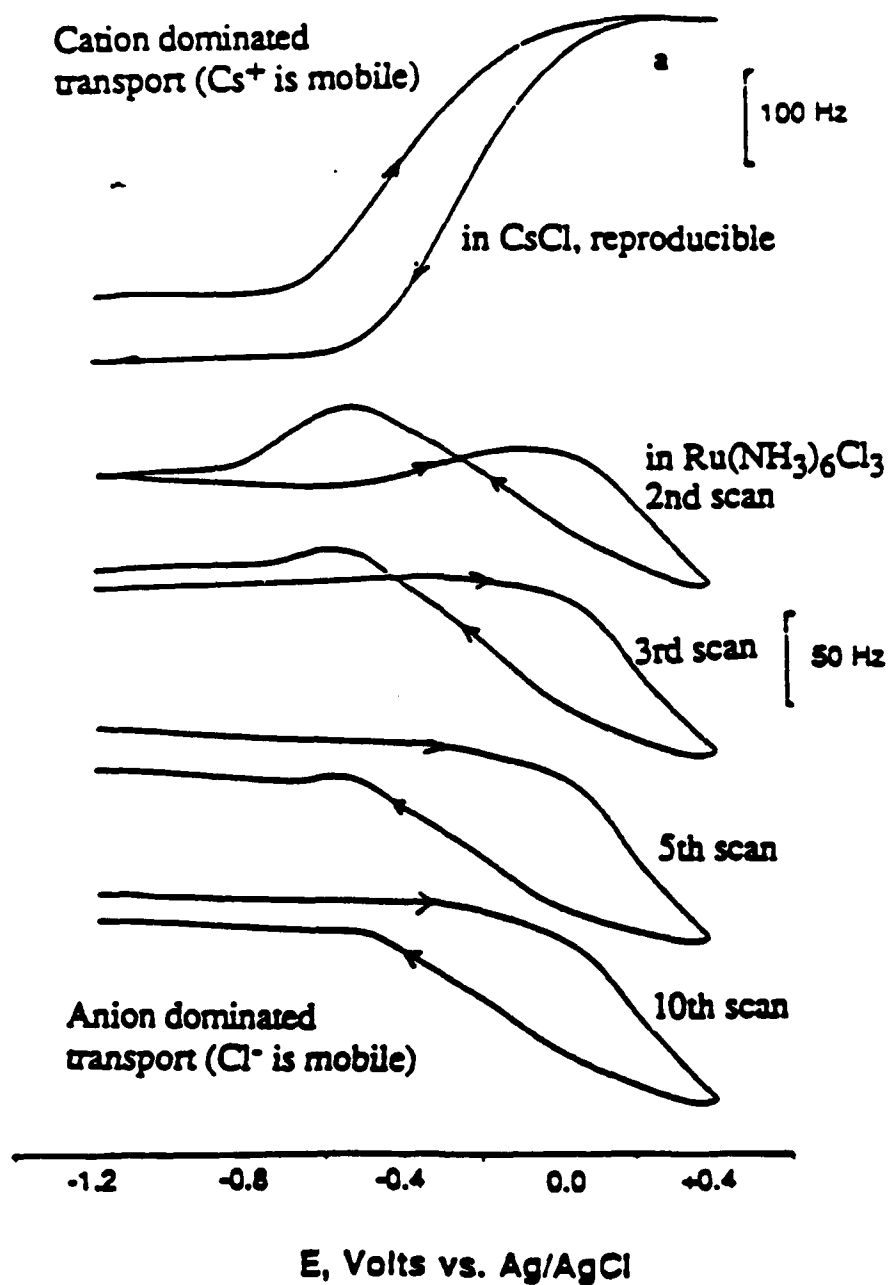


Gravimetric responses of the PP-CDS film as potential is switched between -1.0V and +0.2V

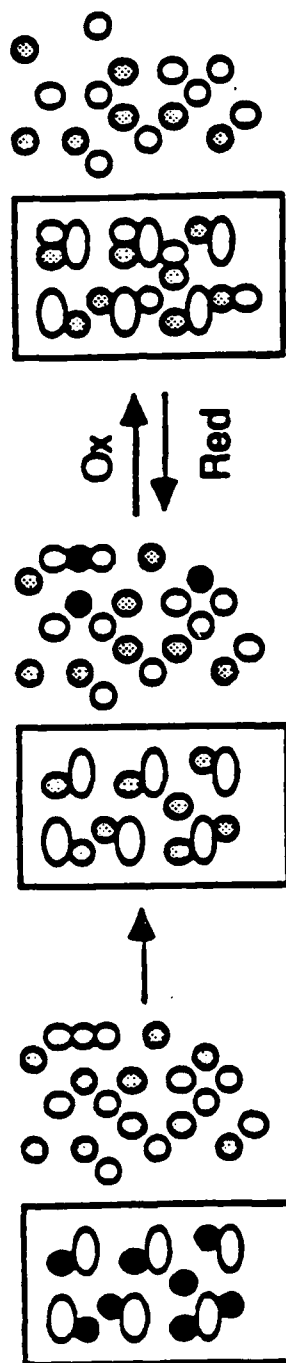
Raman Spectra During Electrochemical Switching



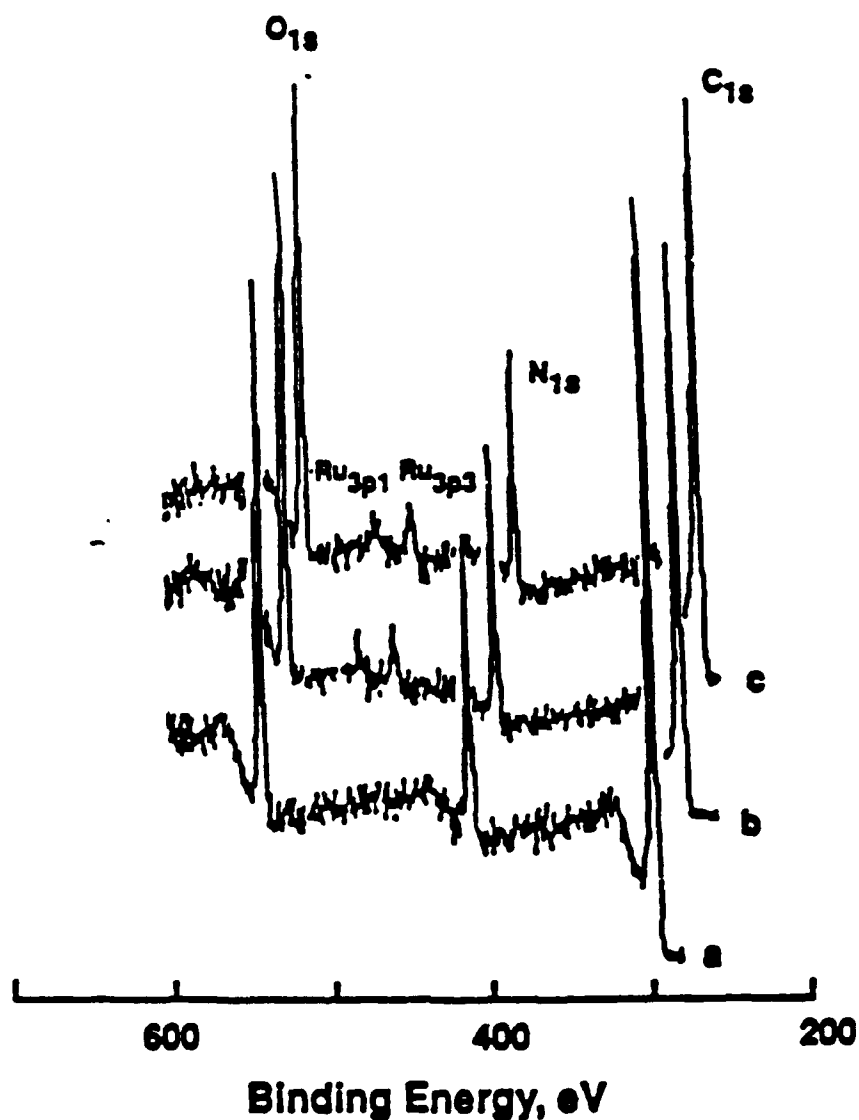
EQCM Frequency Changes During Redox Switching of Polypyrrole in $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$



Cation Exchange → Immobilization of Ru → anion transport



○ CDS
 ● Cs cations
 ⊙ Ru complex cations
 ○ Cl anions

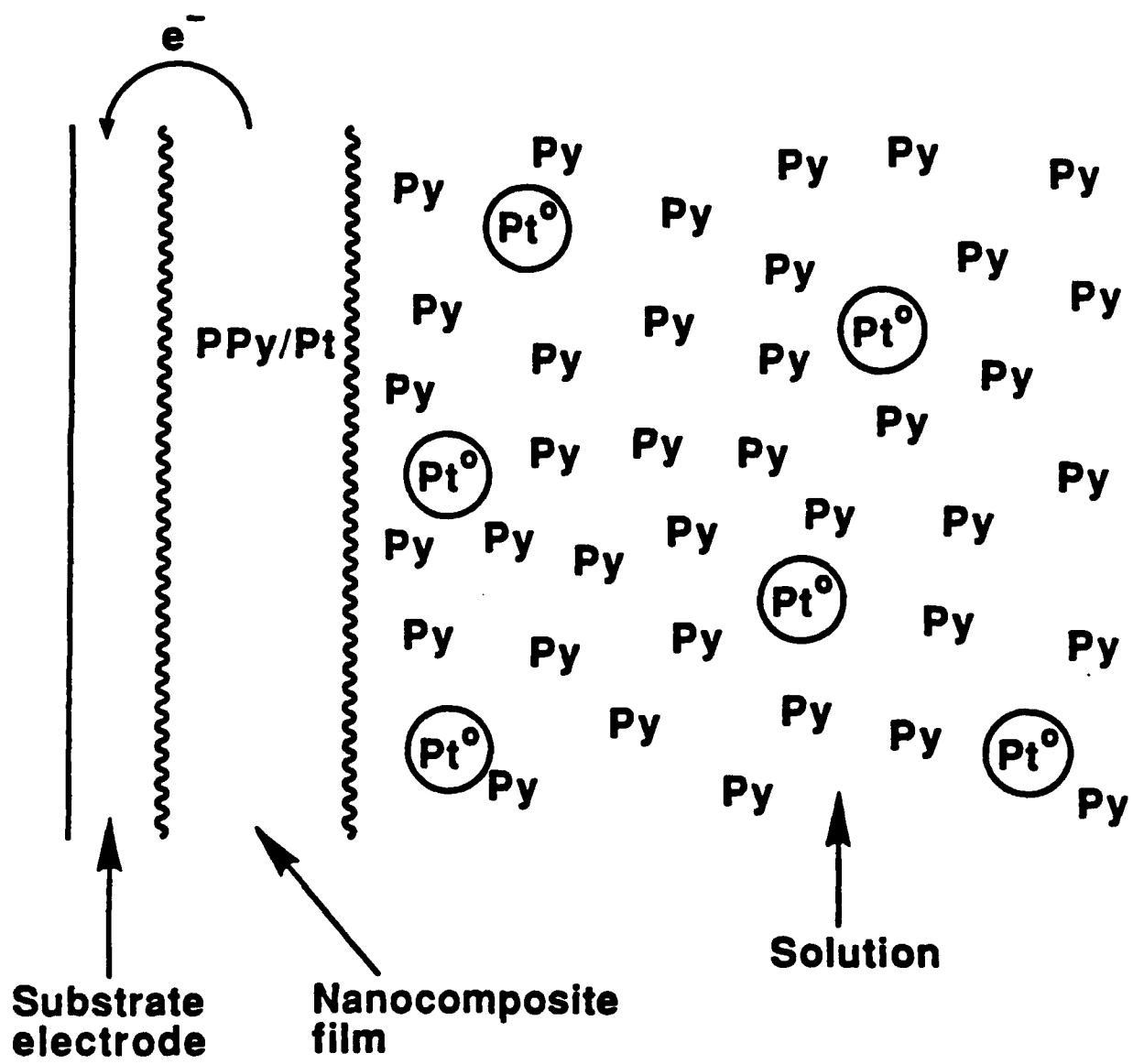
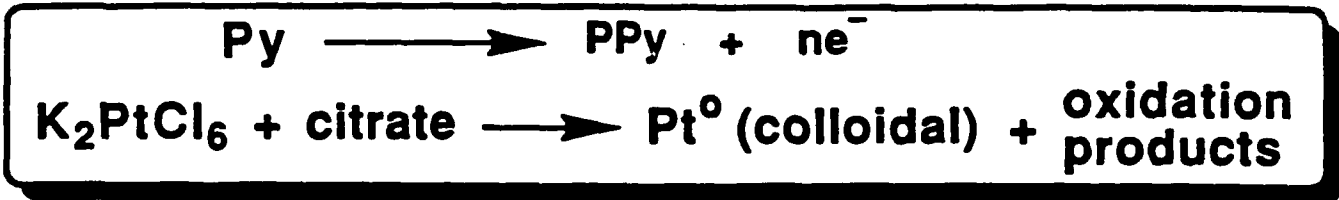


ESCA Spectra of Poly(pyrrole cyclodextrintetradecasulfate)

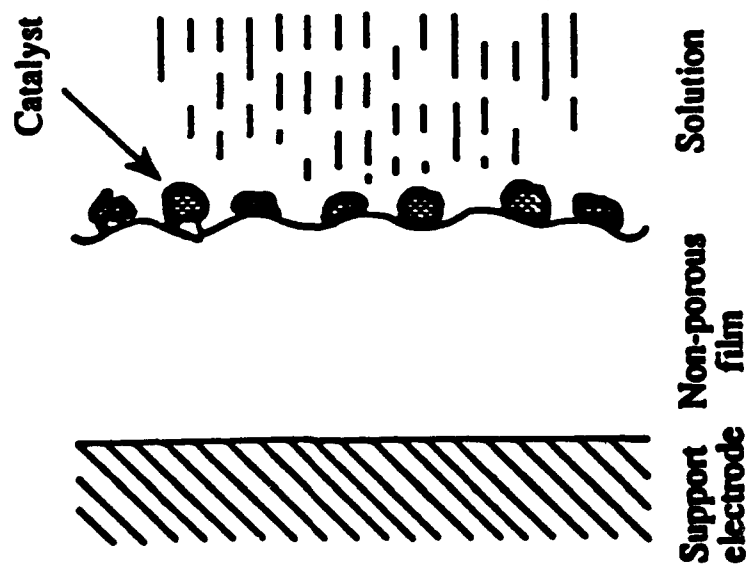
- a. Cycled In CsCl
- b. Subsequently cycled 50 times In $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$
- c. Subsequently cycled 50 times In CsCl

load polymer
Ru entrapment
in the
in cyclodextrin

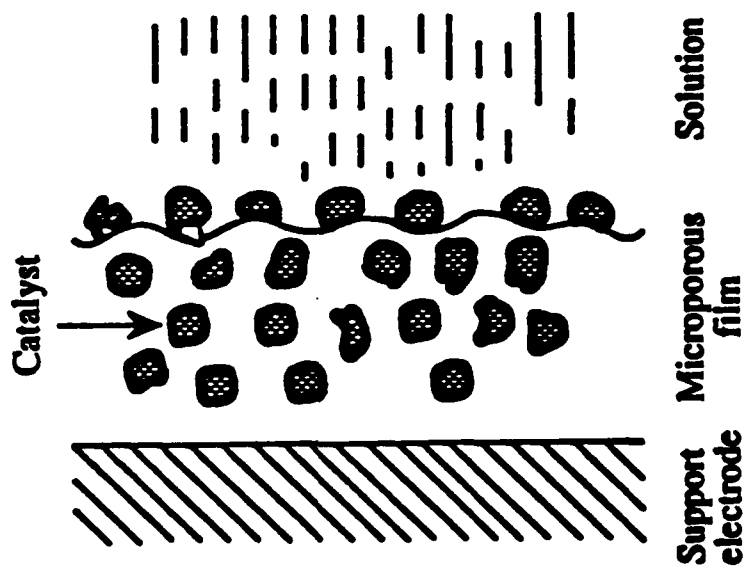
hydrolysis of py & polymerization of Pt colloids
Pt entrapment in polypyrrole



Surface-confined Catalyst



3-D Situation



Polypyrrole/Platinum Nanocomposites

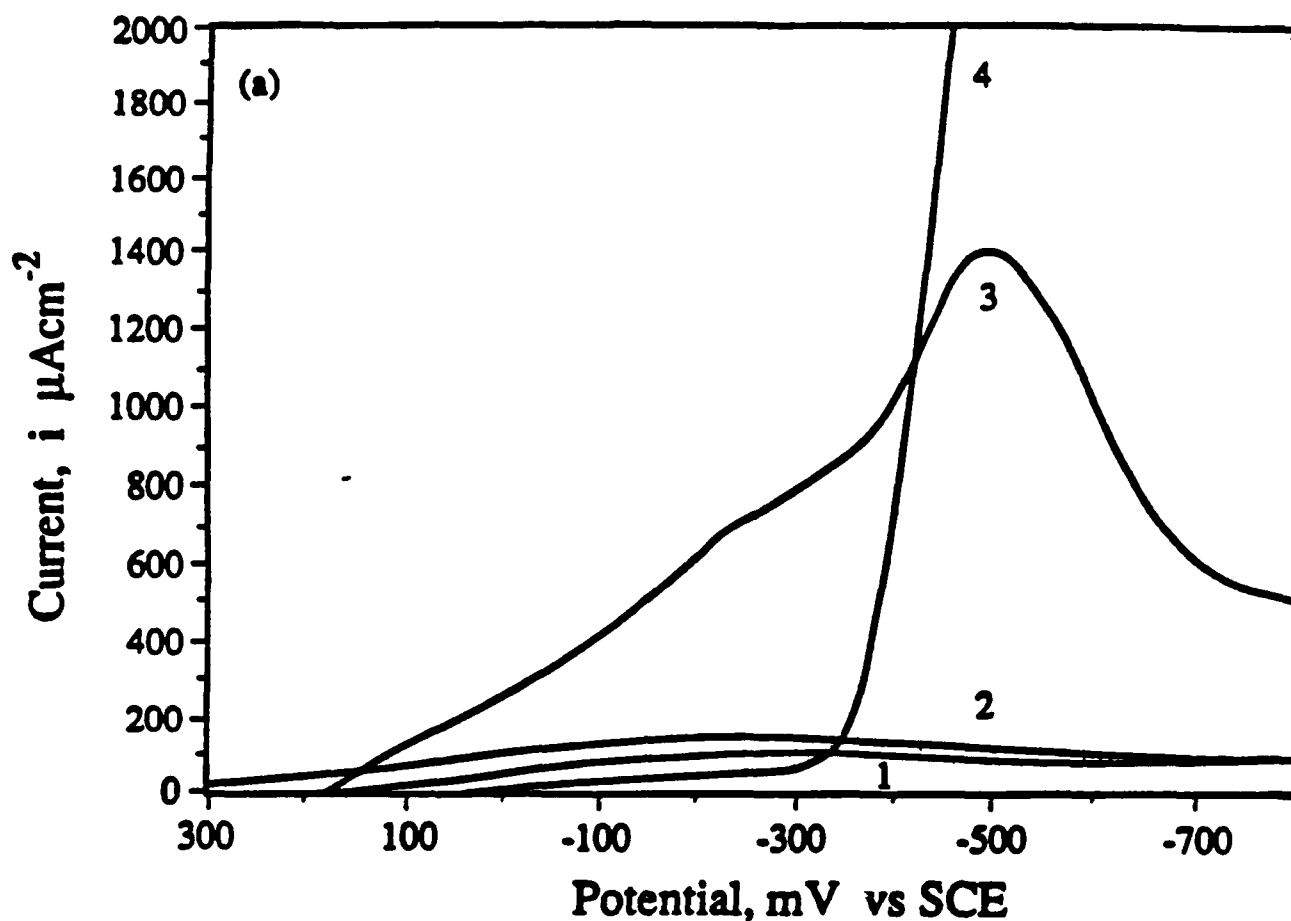


POLYPYRROLE/Pt NANOCOMPOSITES

New electrode materials tested with fuel cell
reaction candidates:

II-D-60





Electrocatalytic Behavior for Hydrogen Evolution Reaction

1. Polypyrrole
2. Polypyrrole/Platinum (on surface)
3. Polypyrrole/Platinum (three-dimensional distribution)*
4. Platinum Metal

Polypyrrole/Platinum Nanocomposites

Homogeneous vs. Heterogeneous Catalysis

- Catalyst particles dispersed in solution yield electrodes with greater dimensionality compared to surface-confined analogues
- 3-D distribution of Pt^0 within microporous polypyrrole transforms a heterogeneous catalyst system into a more homogeneous system
- Large surface area of polypyrrole reduces reaction overpotentials

Materials Savings

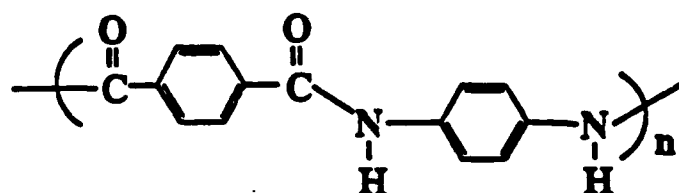
- A polypyrrole/ Pt^0 nanocomposite (Pt content: 0.84 mg/cm^2) is comparable in catalytic activity to a Pt foil (Pt content: 23.6 mg/cm^2) with same film thickness (14 microns)
- This translates to a reduction in Pt usage of 96%

Stability of Polypyrrole...

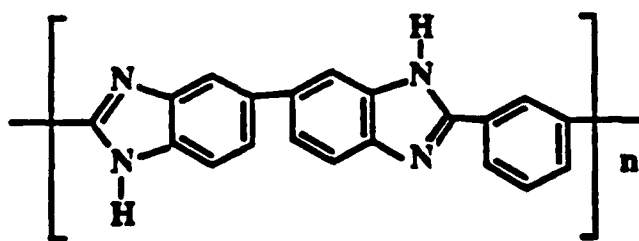
Compare to
std PtT #1...

High Aspect Ratio Polymers:

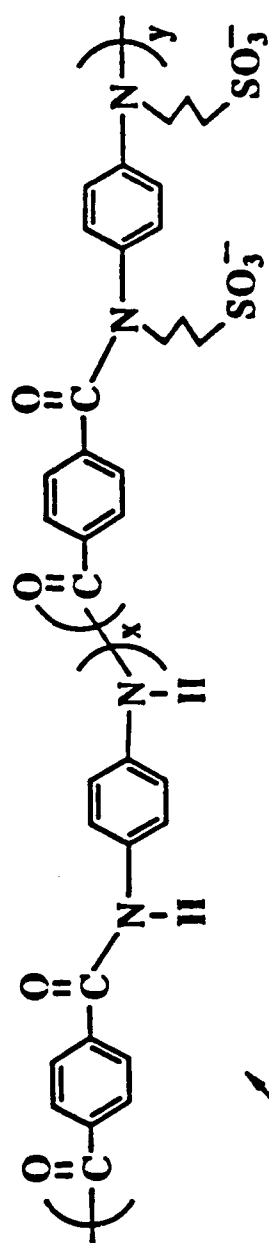
- ◆ All Aromatic
- ◆ Thermally Stable
- ◆ Chemically Resistant
- ◆ Processing Difficulties



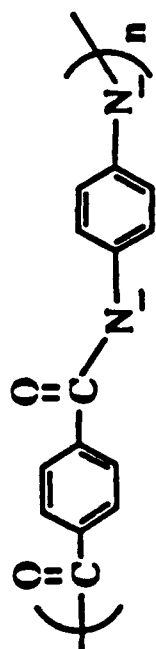
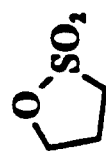
Kevlar



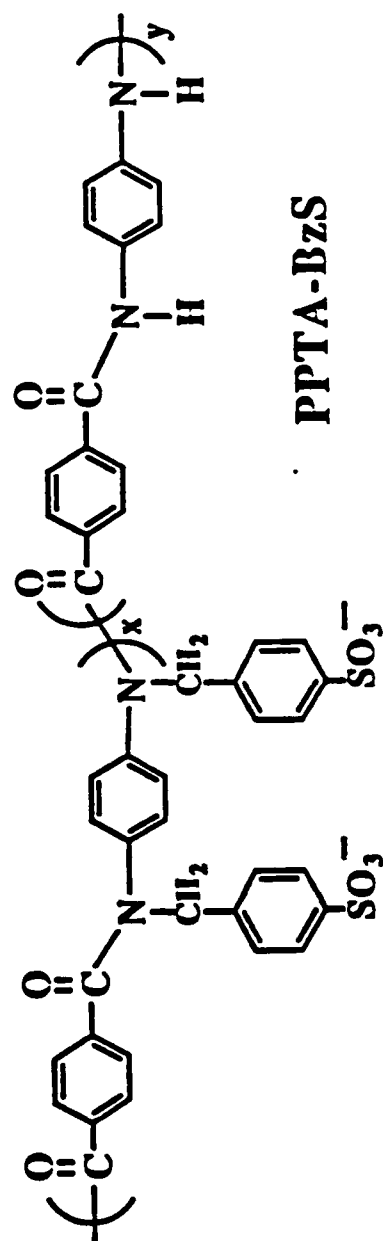
PBI



PPTA-PS



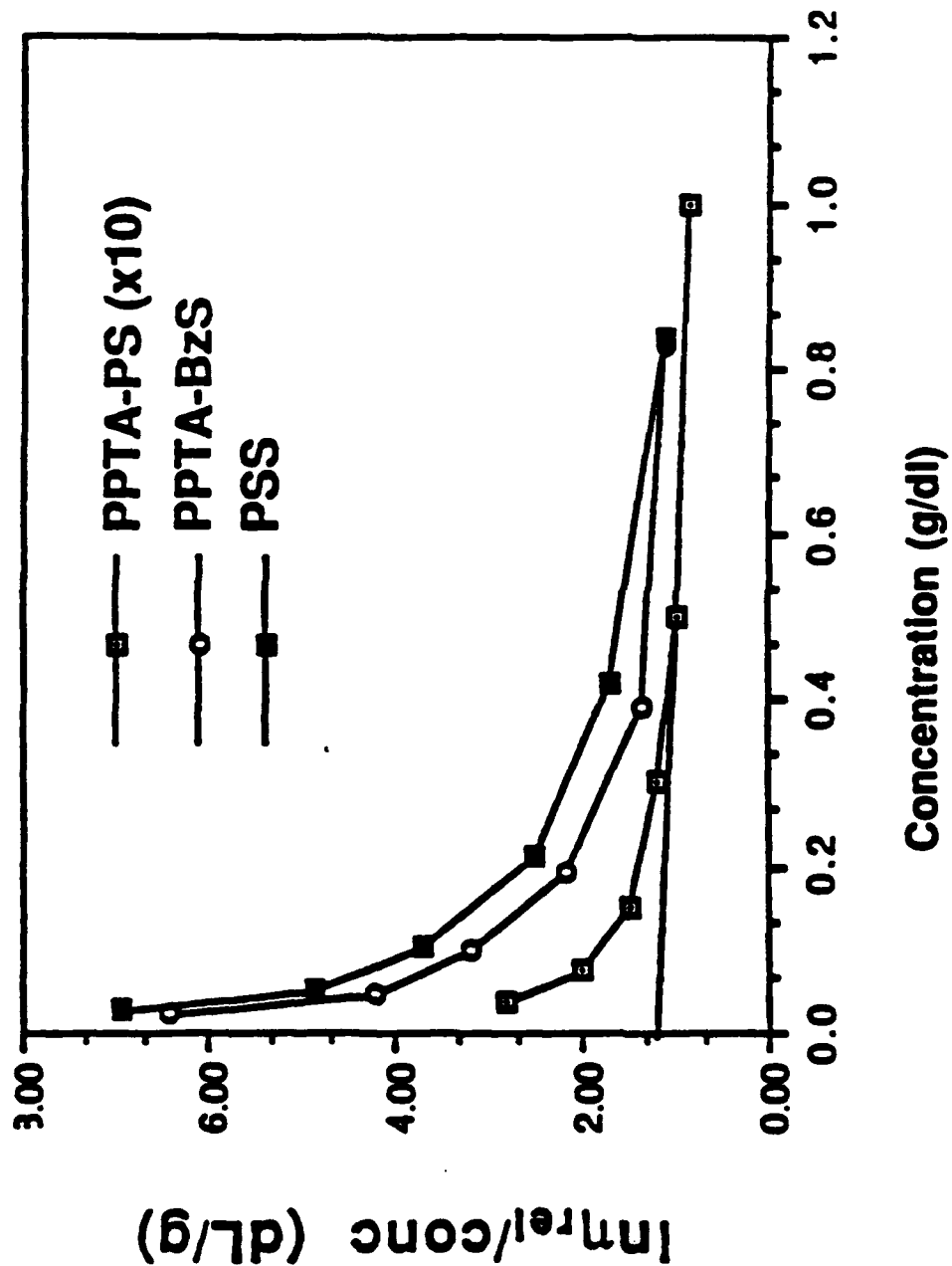
II-D-64



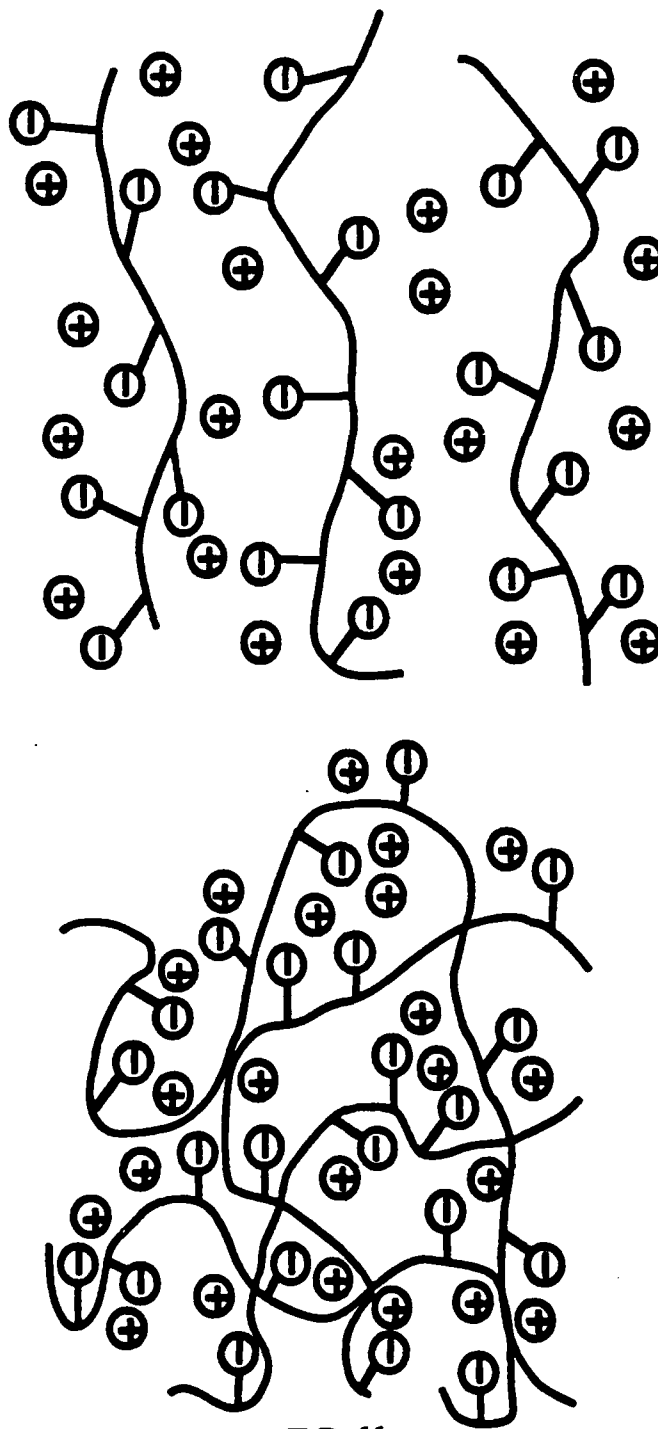
PPTA-BzS

Kevlar
derivatives

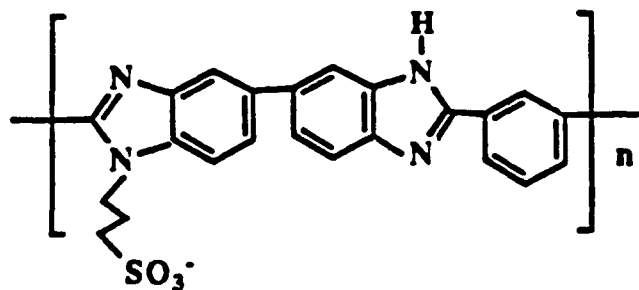
Viscosity Results for Aqueous
Derivatized Kevlar Solutions



The Polyelectrolyte Effect

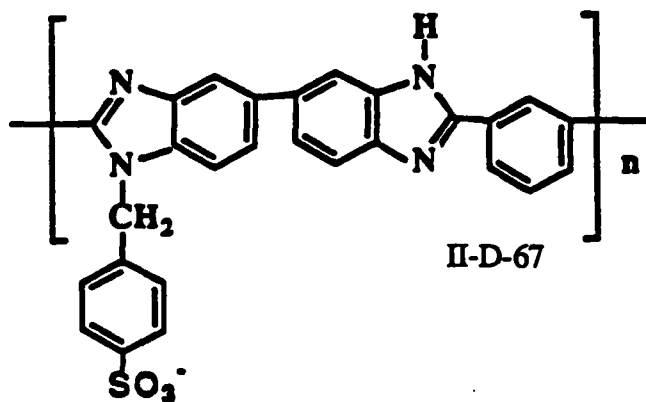
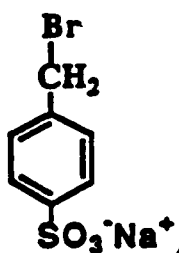
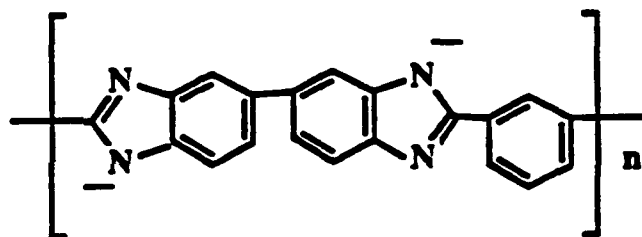
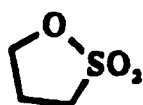


II-D-66



PBI-PS

Celazole

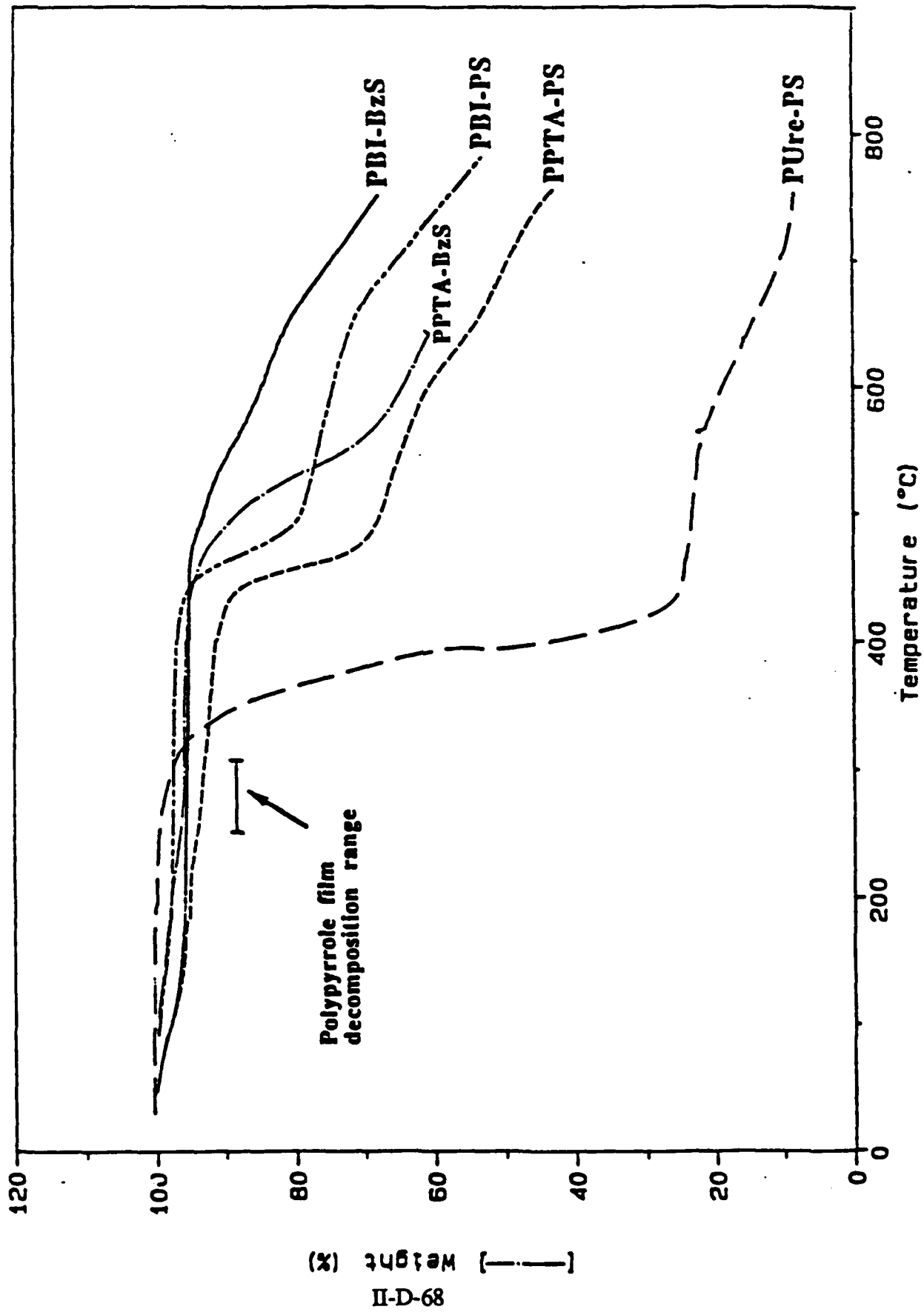


PBI-BzS

II-D-67

in N₂

TGA



II-D-68
[—] Weight (%)

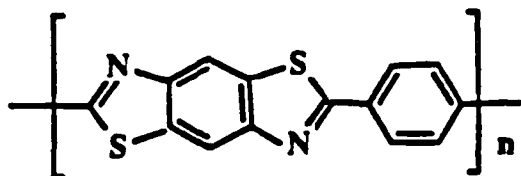
**Thermal Stability of
Polypyrrole/Polyelectrolyte Composites**

Film Type (sulfonate type)	σ ($\Omega \cdot 1\text{cm}^{-1}$)	OTD*($^{\circ}\text{C}$) (polyelectrolyte)
PP/Tos (Ar)	35.2	275
PP/PSS (Ar)	4.8	250 (460)
PP/HE-300 (Al)	0.3	300 (350)
PP/PAMPS (Al)	0.6	275
PP/PPTA-PS (Al)	0.3	300 (450)
PP/SPEEK (Ar)	3.9	250 (475)
PP/PPTA-BzS (Ar)	9.8	300 (460)
PP/PUre-PS (Al)	0.1	300 (350)

* Temperature at onset of thermal degradation.

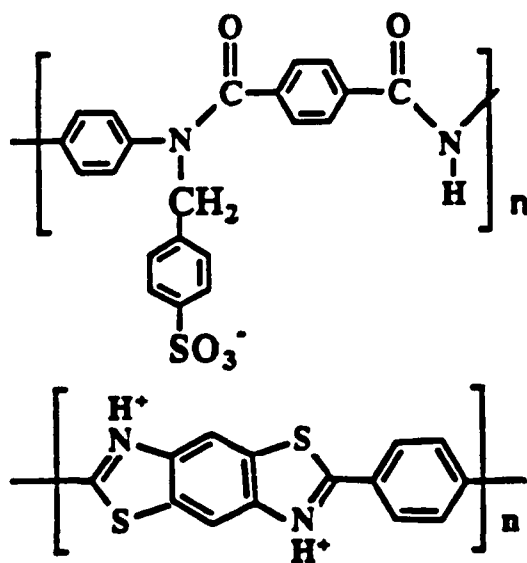
Ternary Solutions

◆ processable to molecular composites

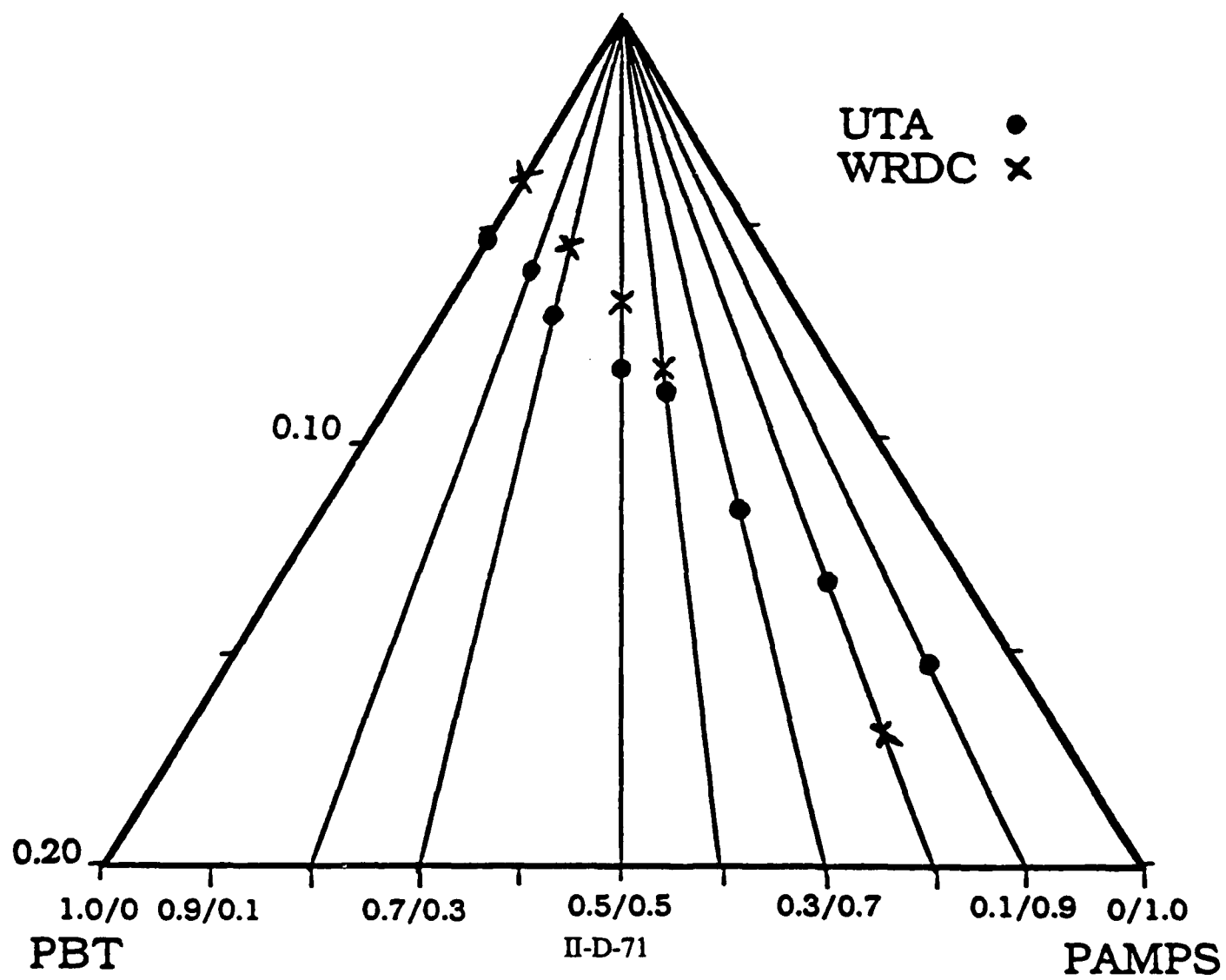


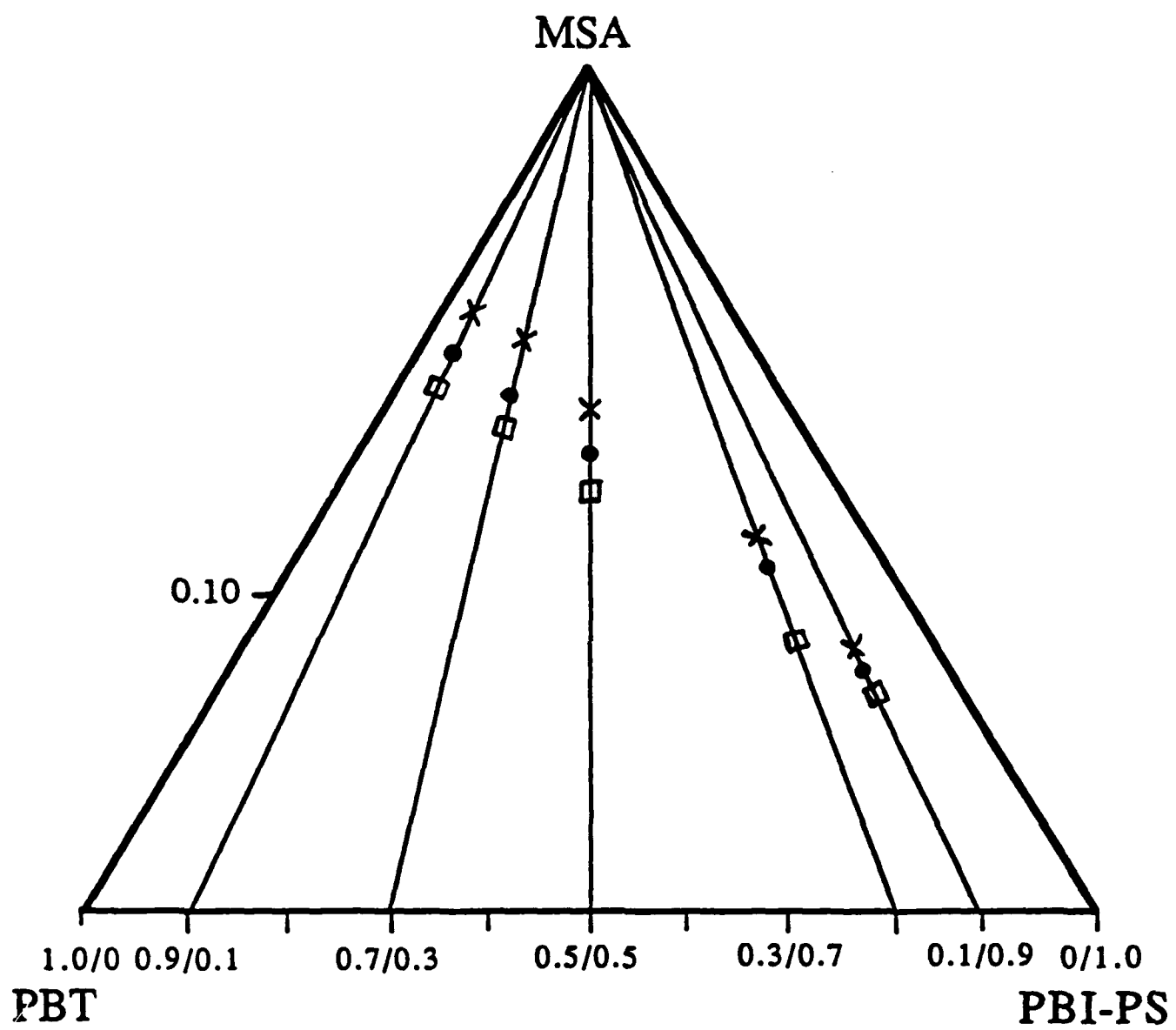
PBT

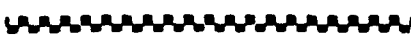
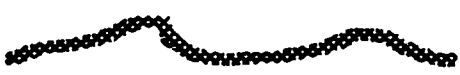
MSA, PPTA-BzS



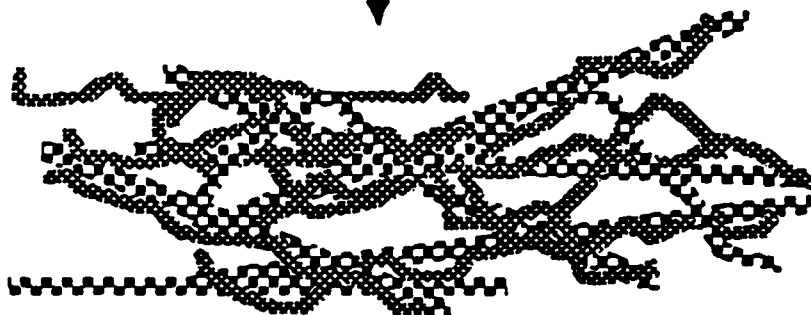
Isotropic PPTA-BzS/PBT/MSA solution.





 PBT
 Polyelectrolyte
Miscible PBT/Polyelectrolyte/MSA Blend

syringe into aqueous FeCl_3



**Oriented, swollen PBT/polyelectrolyte
complex gel containing oxidant.**

Pyrrole monomer
dry



Conducting Multicomponent Molecular Composite

(——— Polypyrrole)

II-D-73



**Polypyrrole
Poly(benzobisthiazole)
Poly(styrenesulfonate)
Molecular Composite Fiber**

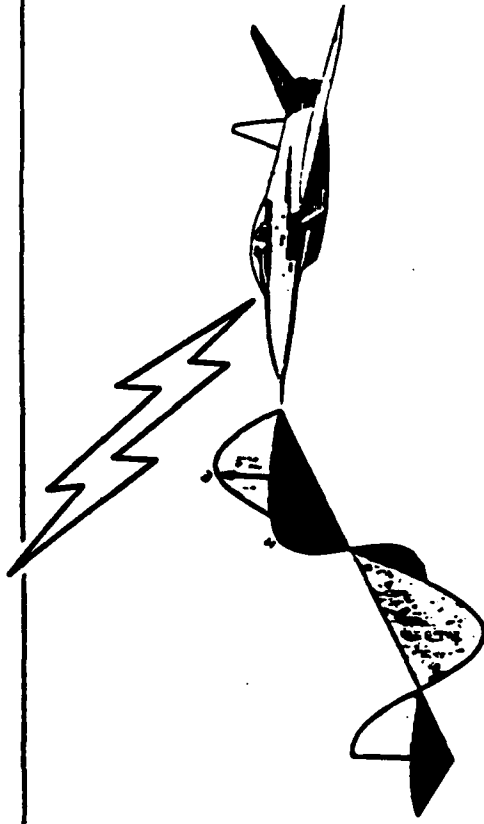
3-4"
length.

$$\sigma = 0.1 \text{ Scm}^{-1}$$

Conducting Polymers

DESCRIPTION

- Improve Processability and Environmental Stability
- Develop a Switchable Ground Plane for Microwave Frequencies
- Integration of Conducting Polymers Into Composite Structures



CONDUCTING POLYMERS COUNTER EM THREATS

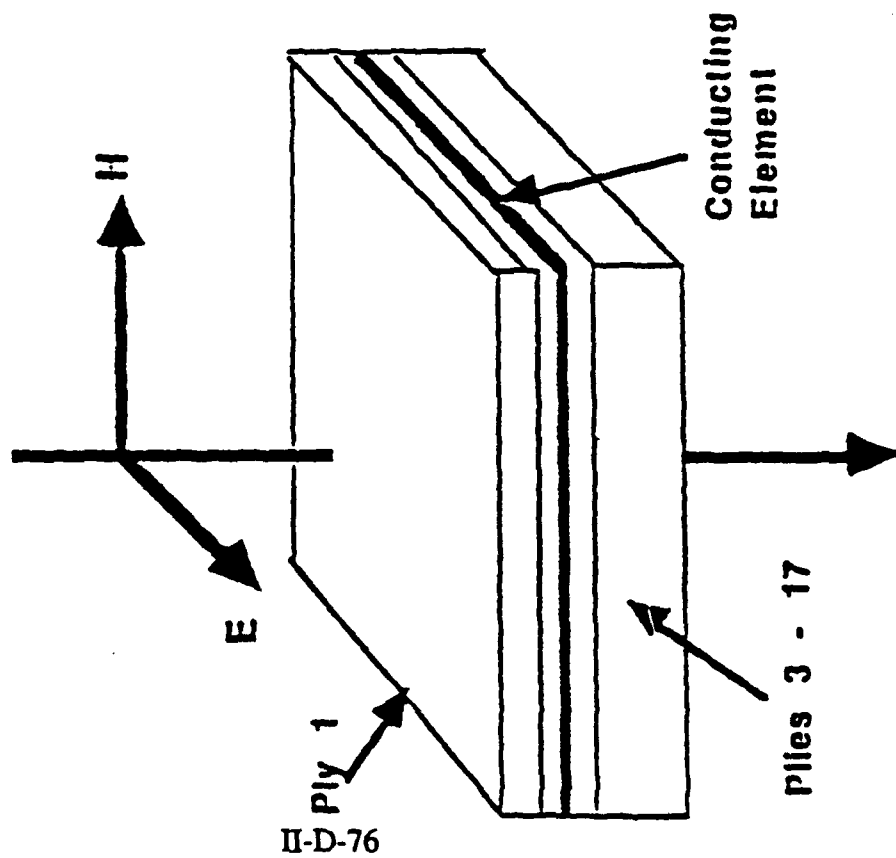
BENEFITS

- Functional Composites (Smart Skins)
 - ✓ Fully Integrated Antennas
- Special Electromagnetic Materials
 - ✓ Compatibility with Composites
 - ✓ Improved Manufacturability
 - ✓ Conductive Coating for Transparencies

STATUS

- Films are Stable in Laminates
- Processing of Large Films and Coated Fabric Established
- Excellent Mechanical Properties Demonstrated
- Switching Over Small Dimensions Demonstrated

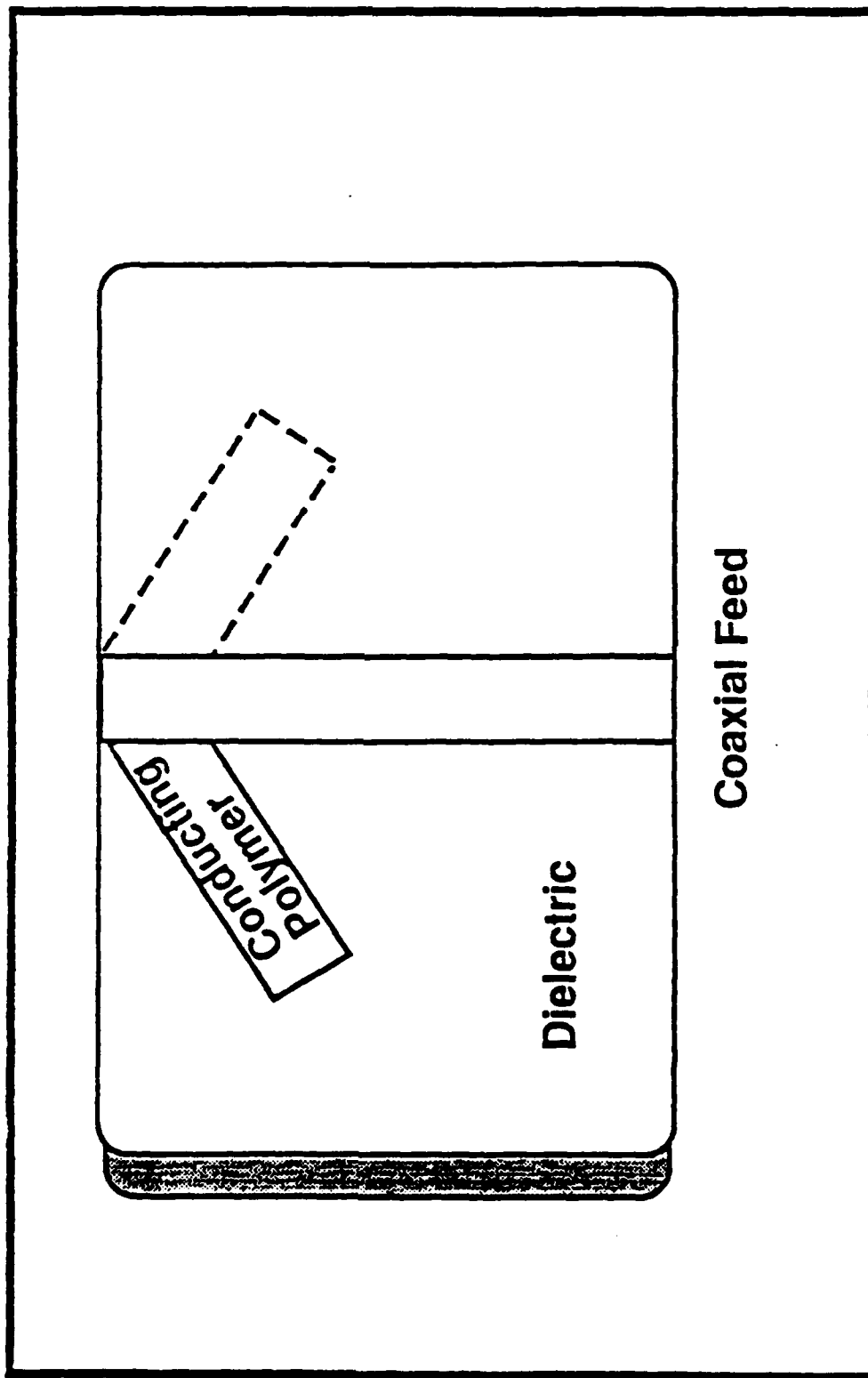
LAYUP FOR ELECTRICAL AND MECHANICAL PROPERTIES OF CONDUCTIVE FILMS IN LAMINATES



CONDUCTIVE ELEMENTS

- Polypyrrole treated quartz fabric (PPO)
- Polypyrrole thin film (PPF)
- Metallized glass fabric (MGF)
- Metallized kapton (MK)
- Perforated metallized kapton (PMK)

CONDUCTING POLYMER DIPOLE ANTENNA



II-D-77

ANTENNA PERFORMANCE VS CONDUCTIVITY

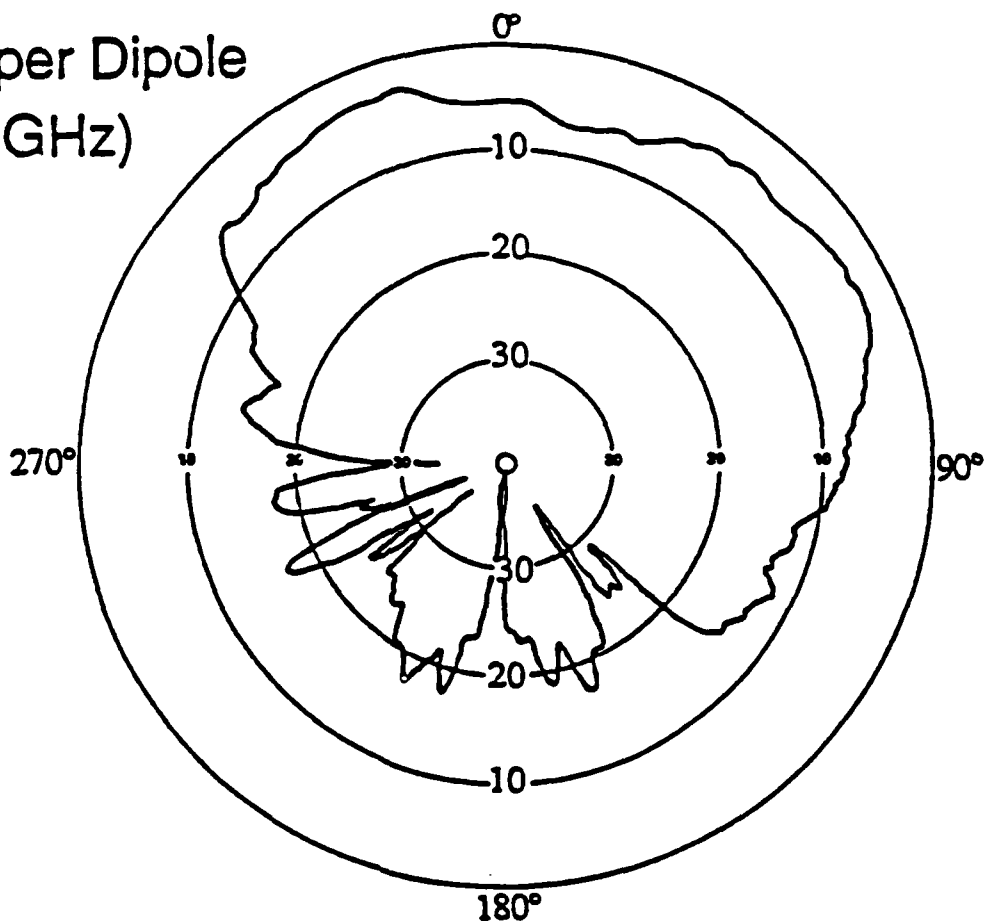
Conductivity	Input Impedance	Efficiency	Gain (max)		Δ Gain	
$\frac{1}{\Omega} - \text{cm}$	Ω	%	dB	ABS	dB	%
10^4	90.490 + j40.496	98.234	2.11	1.62	-	-
10^3	94.610 + j43.090	94.622	1.94	1.56	0.17	3.7
10^2	110.369 + j50.214	82.792	1.37	1.37	0.74	15.4
10	185.979 + j35.176	48.407	-9.6	.80	3.07	50.62
1	474.376 - j337.397	6.614	-9.67	.11	11.78	93.21

II-D-78

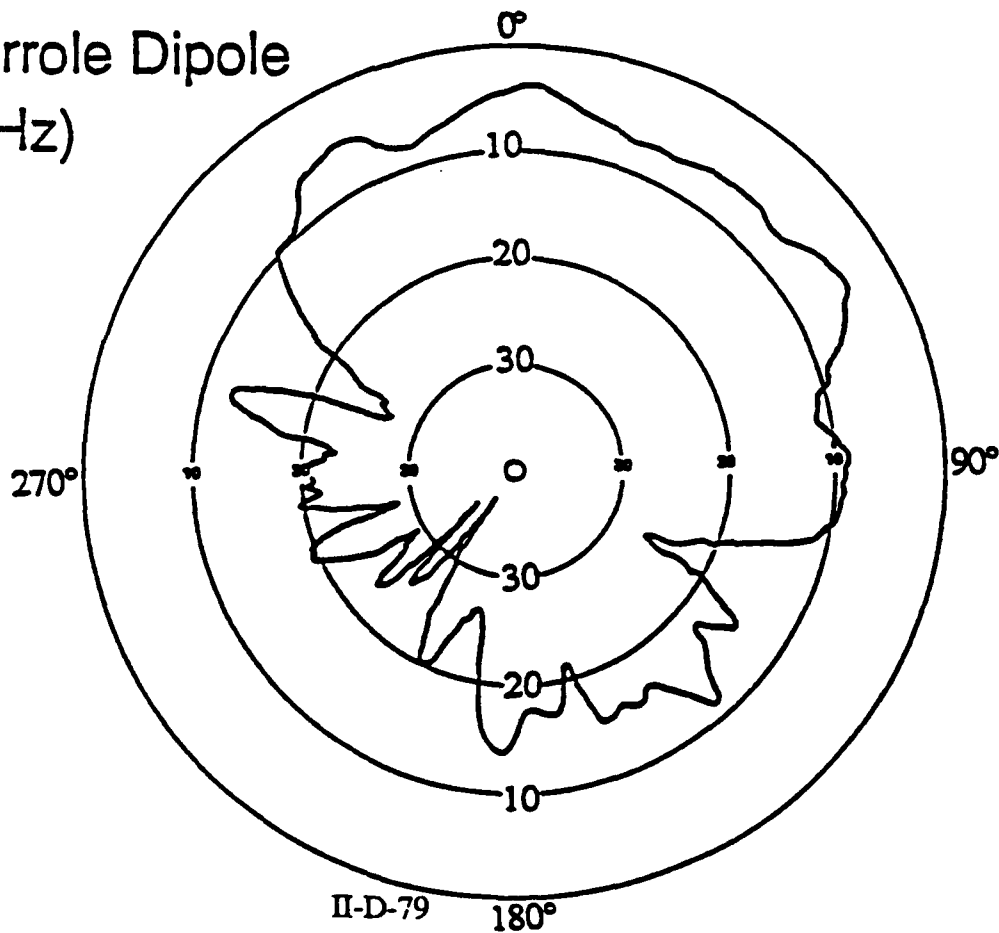
Electrical
performance.

83 \rightarrow 6%
polypropylene still 83%
efficiency. by
but can reduce
switching.

Copper Dipole
(4.0 GHz)



Polypyrrole Dipole
(4.0 GHz)



Polyheterocycle Program Accomplishments

- **Polyheterocycles established as a broad class of conducting polymers with versatile properties**
- **Theoretical modeling of monomer reactivity, monomer/polymer structure and polymer band structure useful in directing experimentation**
- **Soluble low band-gap polyheterocycles applicable to optically transparent, electrically conducting, coatings**
- **Isoregic polyheterocycles contain higher degrees of order than common polyheterocycles with higher ordered systems exhibiting higher electrical conductivities**
- **Ion transport during redox switching of polyheterocycles is controlled by polymer:ion interactions and allow electrically controlled ion specific supply**
- **Transition metal ions can be entrapped within conducting polymer matrices by ion binding processes**
- **Polypyrrole fuel cell electrodes containing colloidal platinum particles for O_2 and H^+ reduction developed**

Polyheterocycle Program Accomplishments

- Both aqueous and solid polymer electrolytes yield conducting polymer batteries with stable charge-discharge and open circuit voltage characteristics
- High aspect ratio water soluble polyelectrolytes developed from thermally stable, rigid polymers retain desirable features of parent polymer
- New polyelectrolytes all form conducting molecular composites with polypyrrole
- Polyelectrolyte/rigid rod interactions increase window of molecular composite processability from ternary solutions
- Polypyrrole/polyelectrolyte surfaces contain reactive pendant anions which can bind proteins and other cationic species
- Polypyrrole films incorporated into epoxy laminates exhibit excellent adhesion and conductivity stability under harsh conditions
- Polypyrrole films successfully used as active element in a radar antenna with >80% efficiency relative to copper films
- Conductivity switching of polypyrrole decreases radar efficiency and detectability

UNIVERSITY OF ILLINOIS

Dr. James Economy

The material from the two University of Illinois presentations is not available.

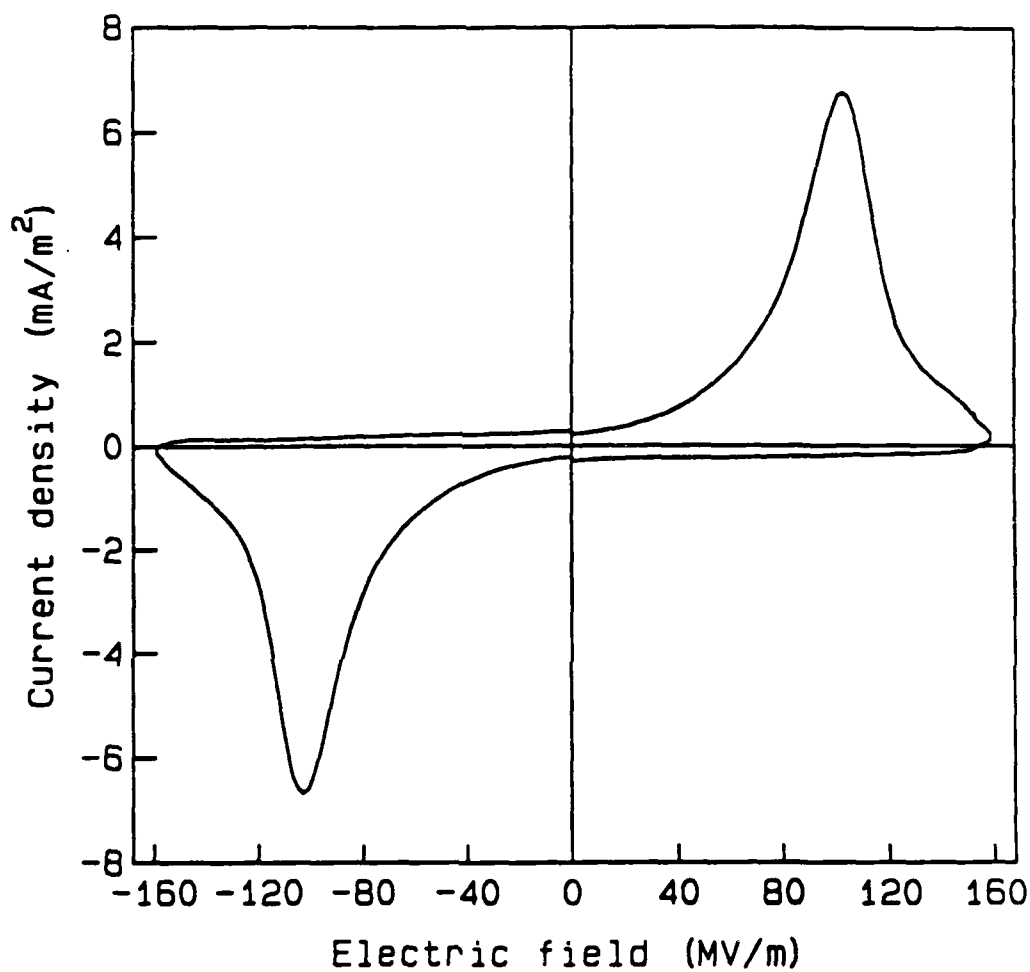
RUTGERS UNIVERSITY

Professor Jerry I. Scheinbeim

Schmitt

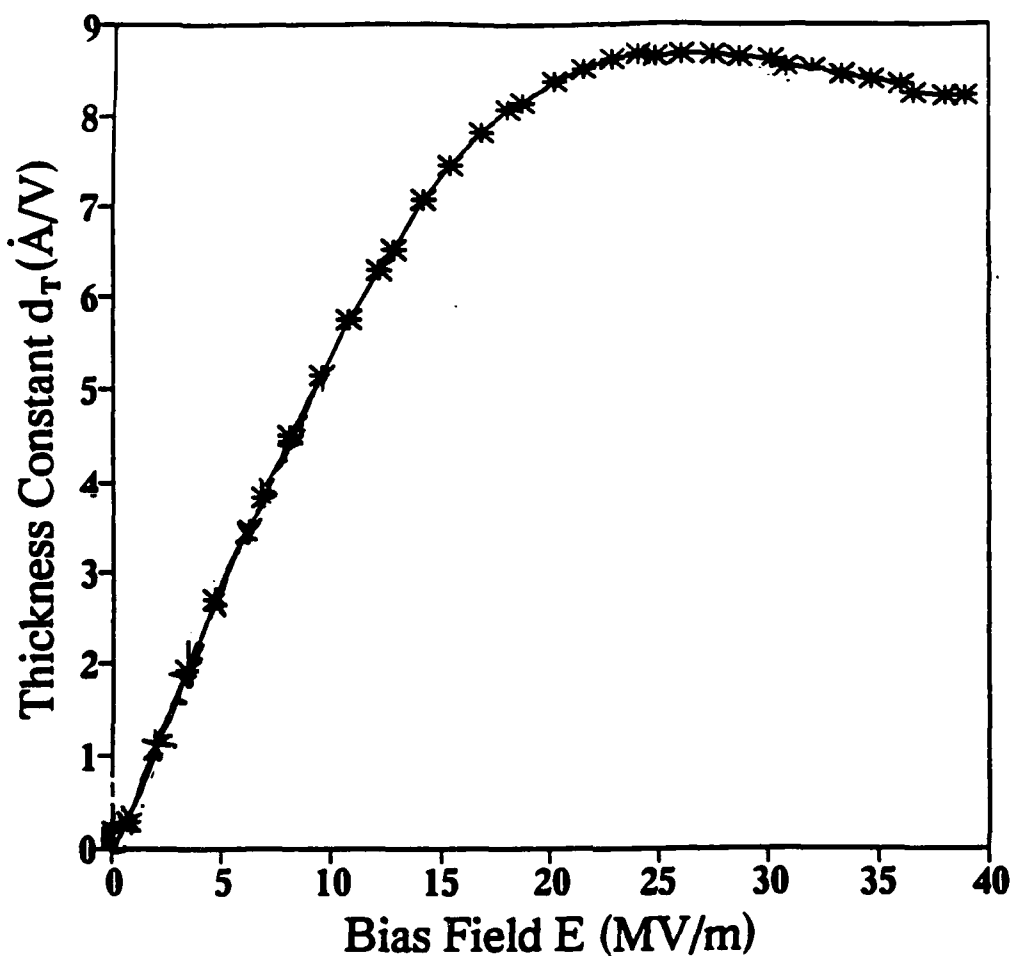
Report

attached



Current density versus electric field for Nylon 5

Polyurethanes



$d_{Tmax} \approx 45 \text{ Å/V}$

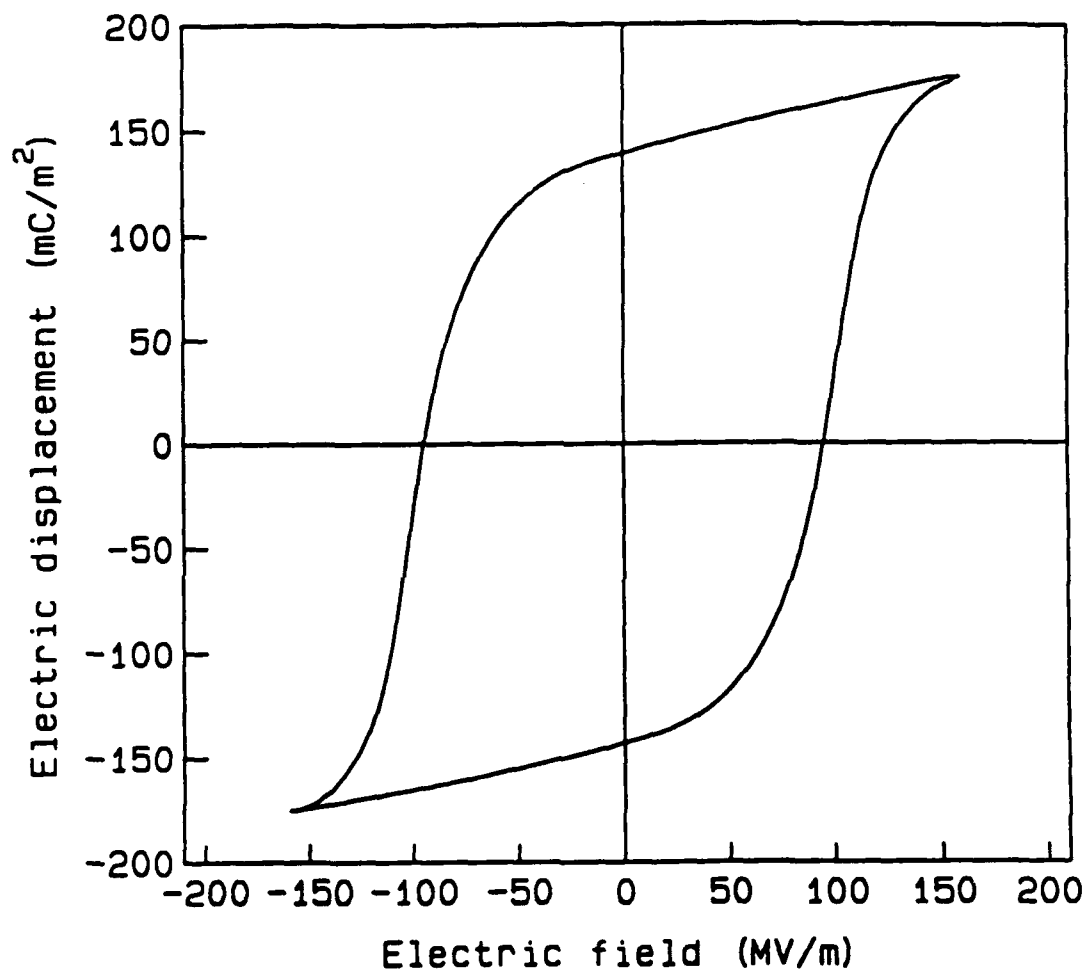
$\epsilon_{max} \approx 20 \%$

$\epsilon_{diel.} \approx 7$

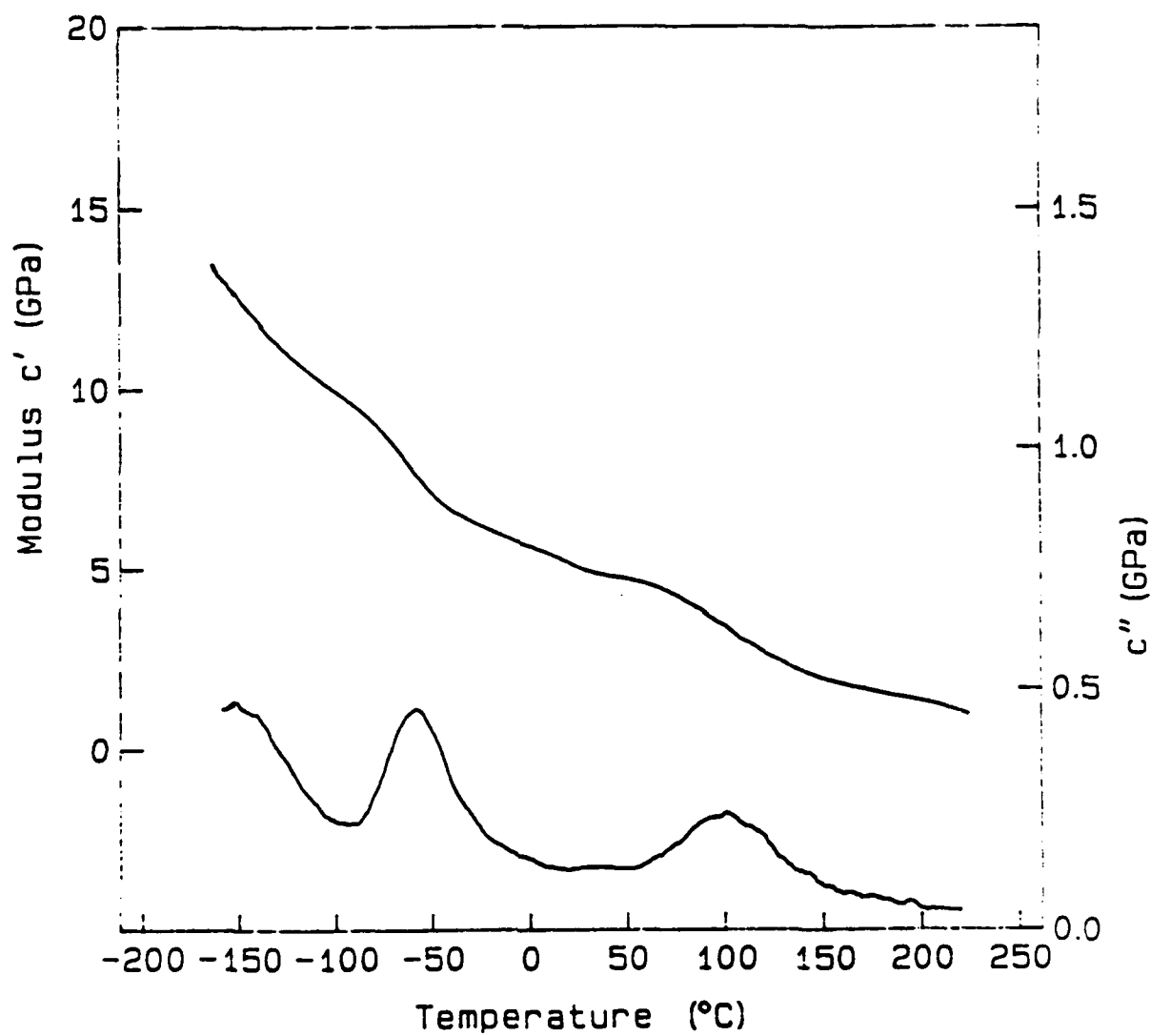
Mod. $\approx 10^7 \text{ N/m}^2$

cost : inexpensive (commercially available at \$3.40/lb.)

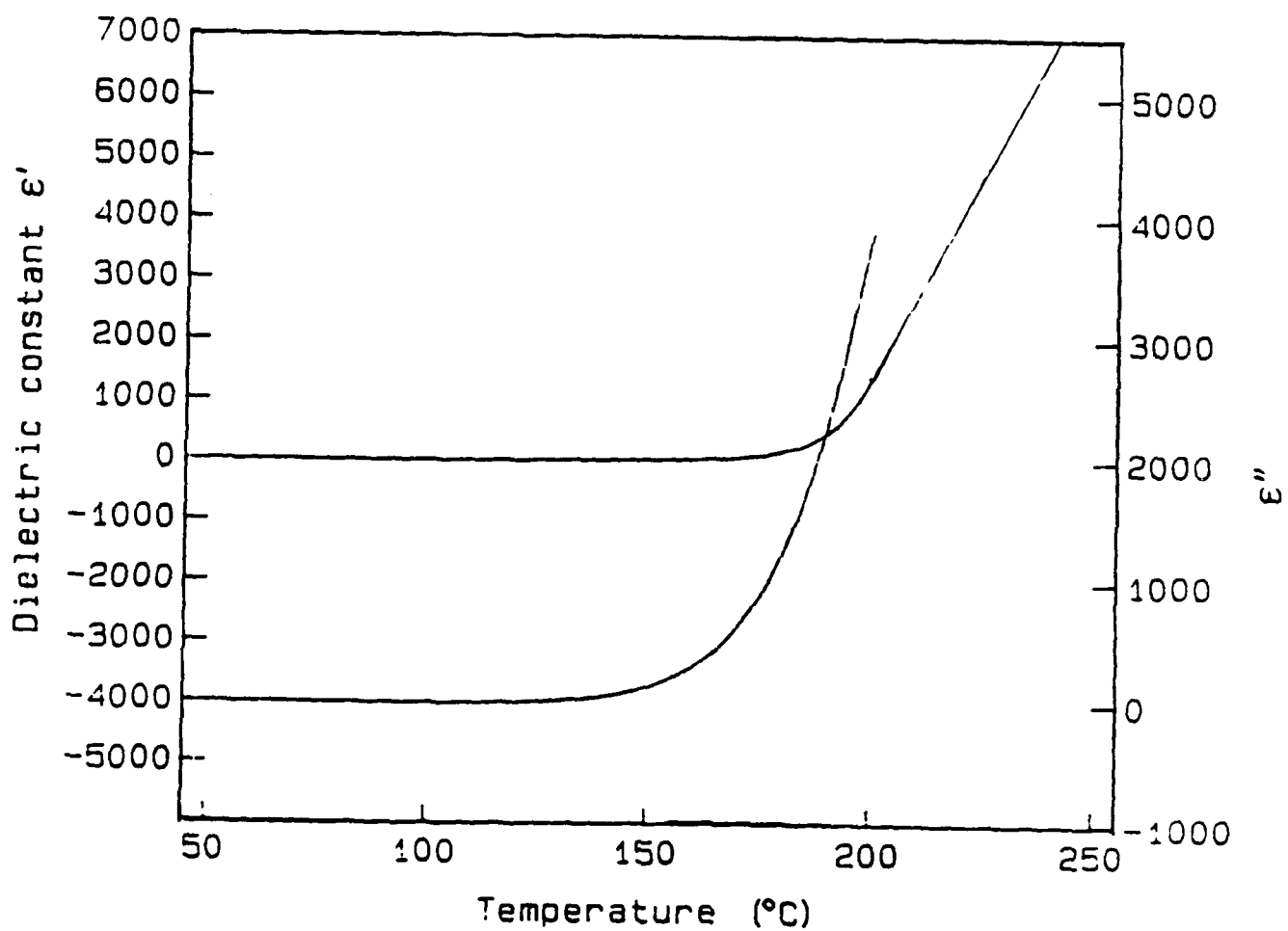
Toughness and impact resistance of an elastomer.



D - E hysteresis loops of Nylon 5

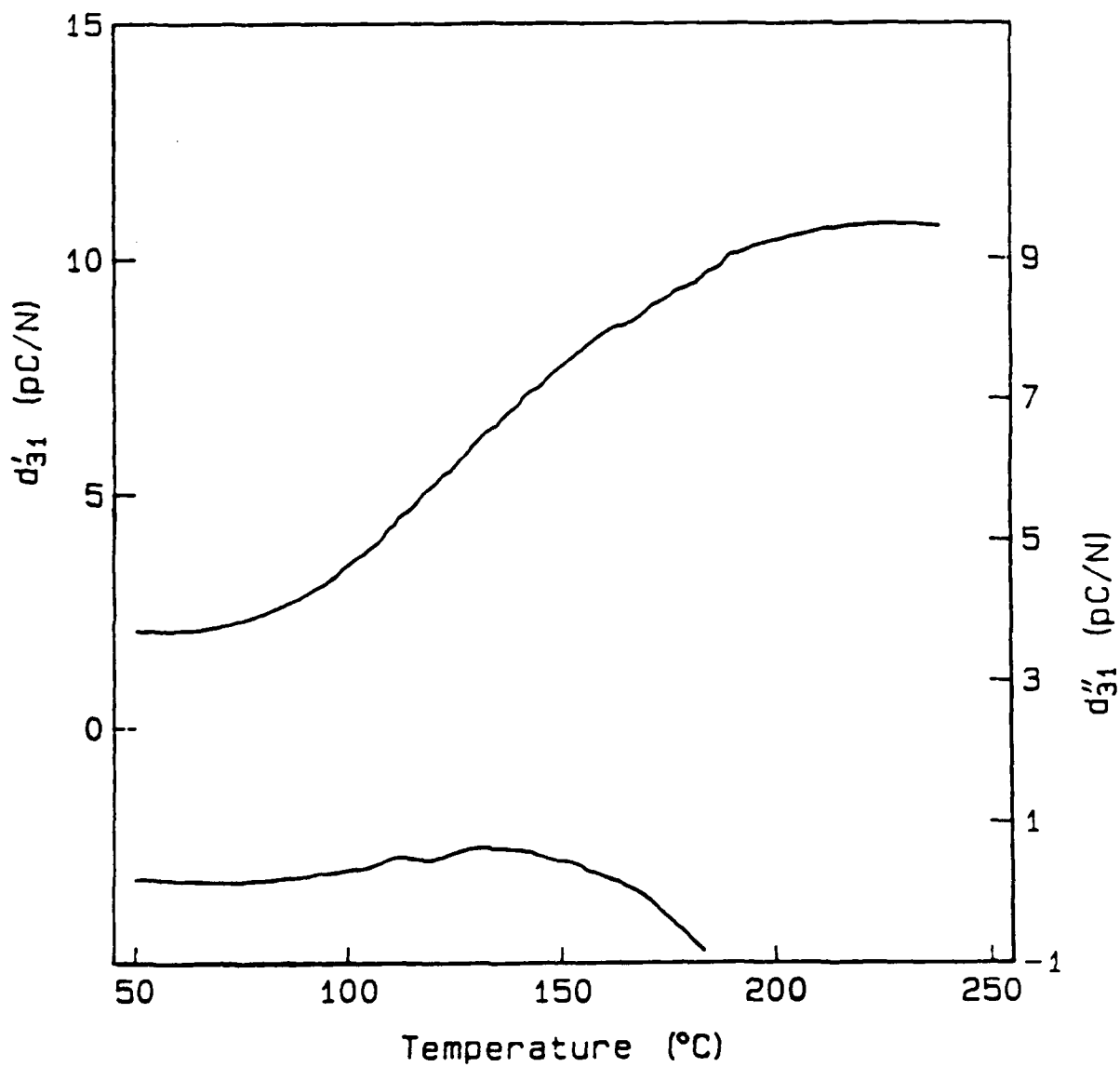


Temperature dependence of the modulus for
samples of Nylon 5 measured at 104 Hz.

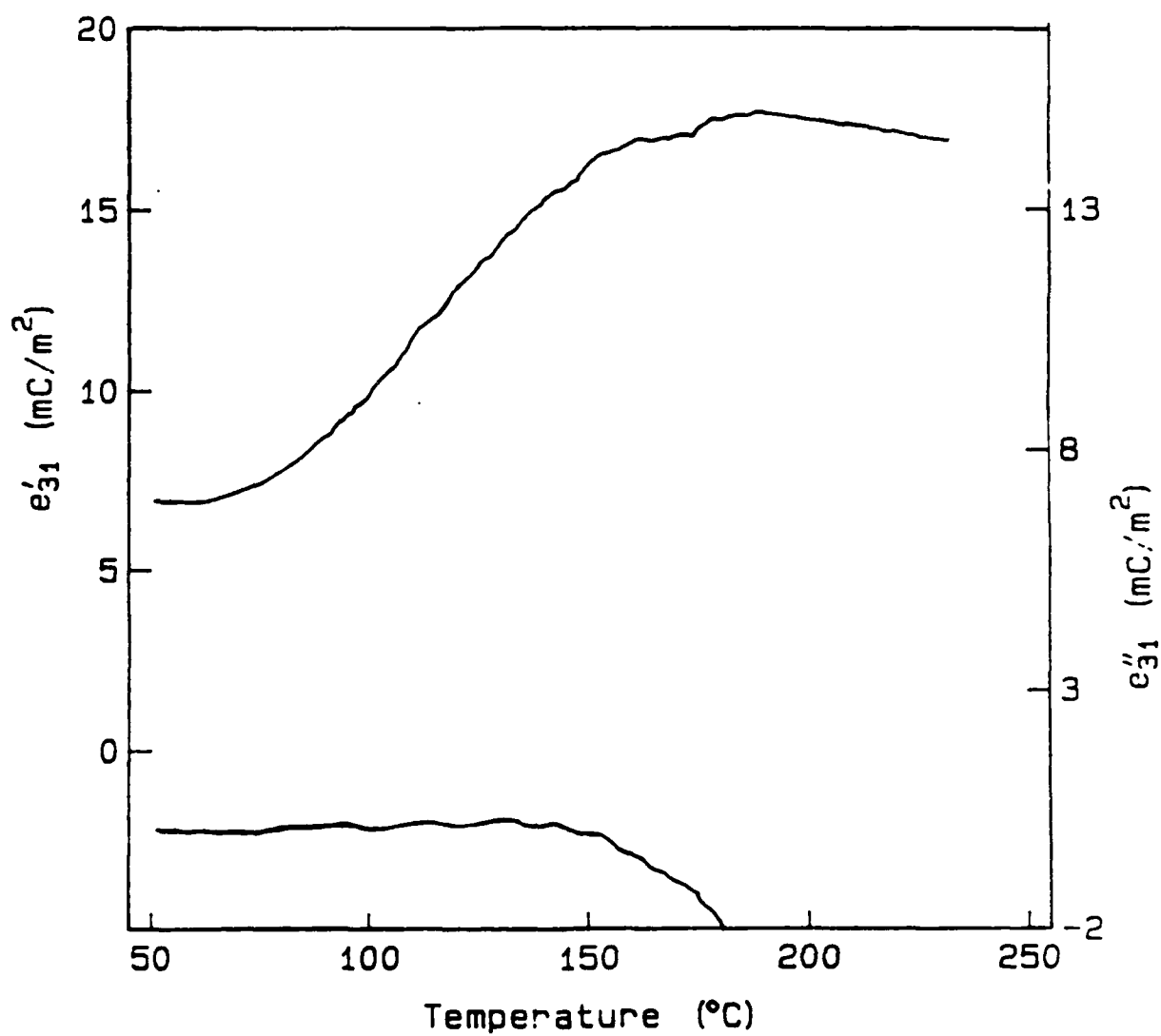


Temperature dependence of dielectric constants
of Nylon 5 measured at 104 Hz

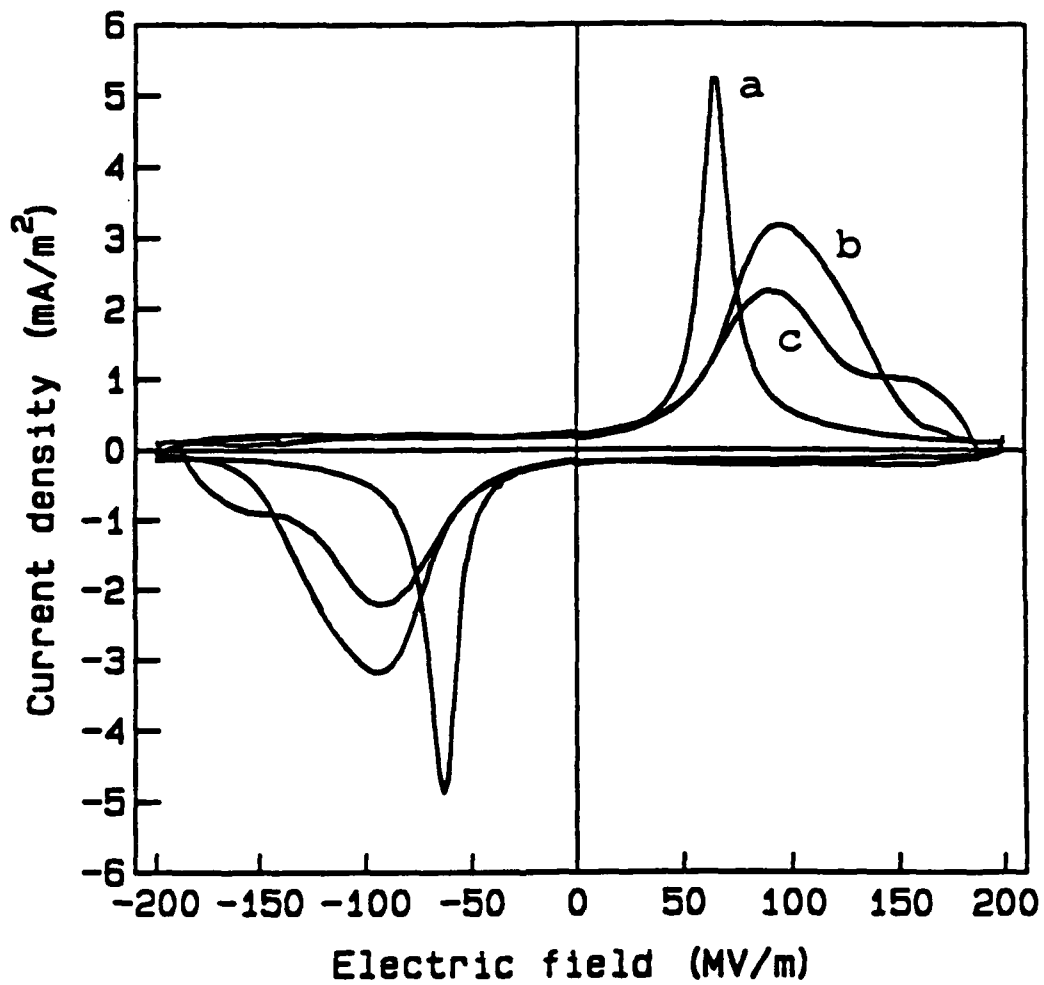
II-F-7



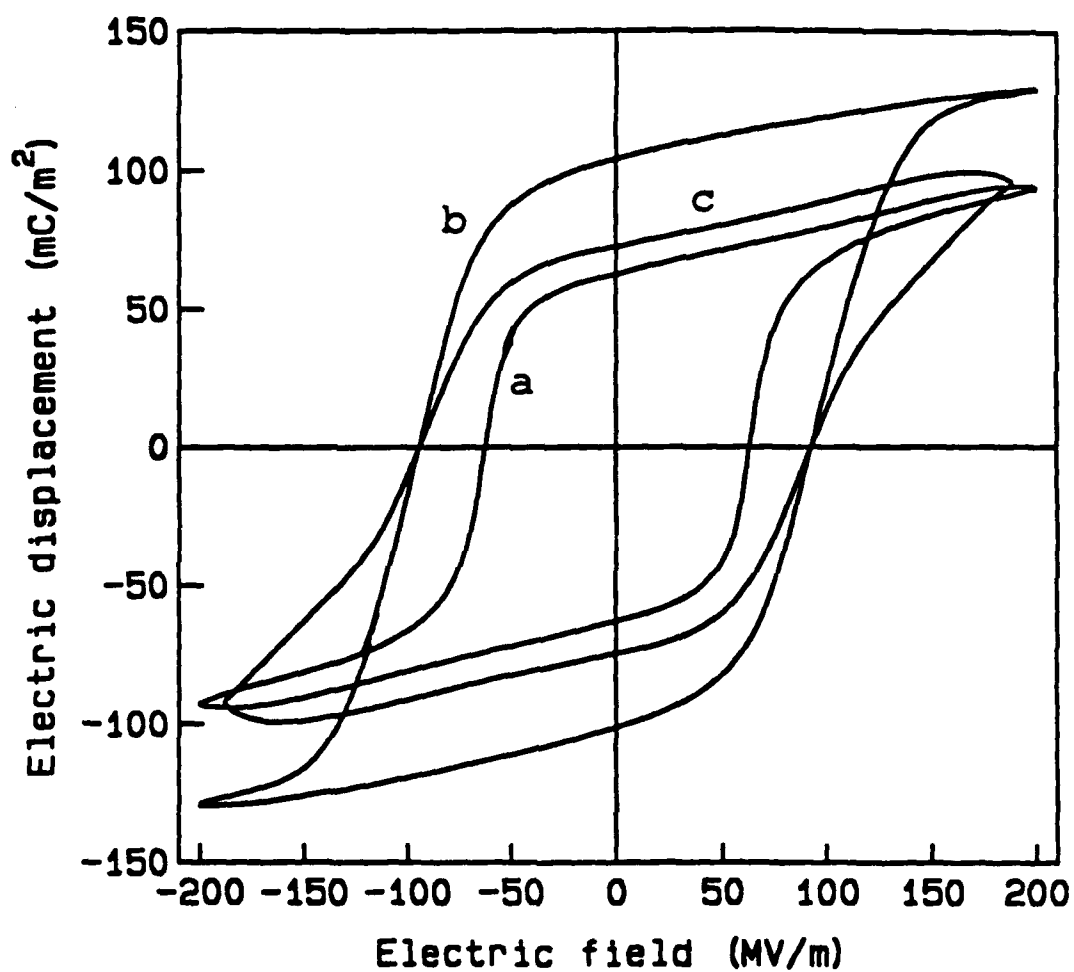
Temperature dependence of the piezoelectric strain constants, d_{31} , of Nylon 5.



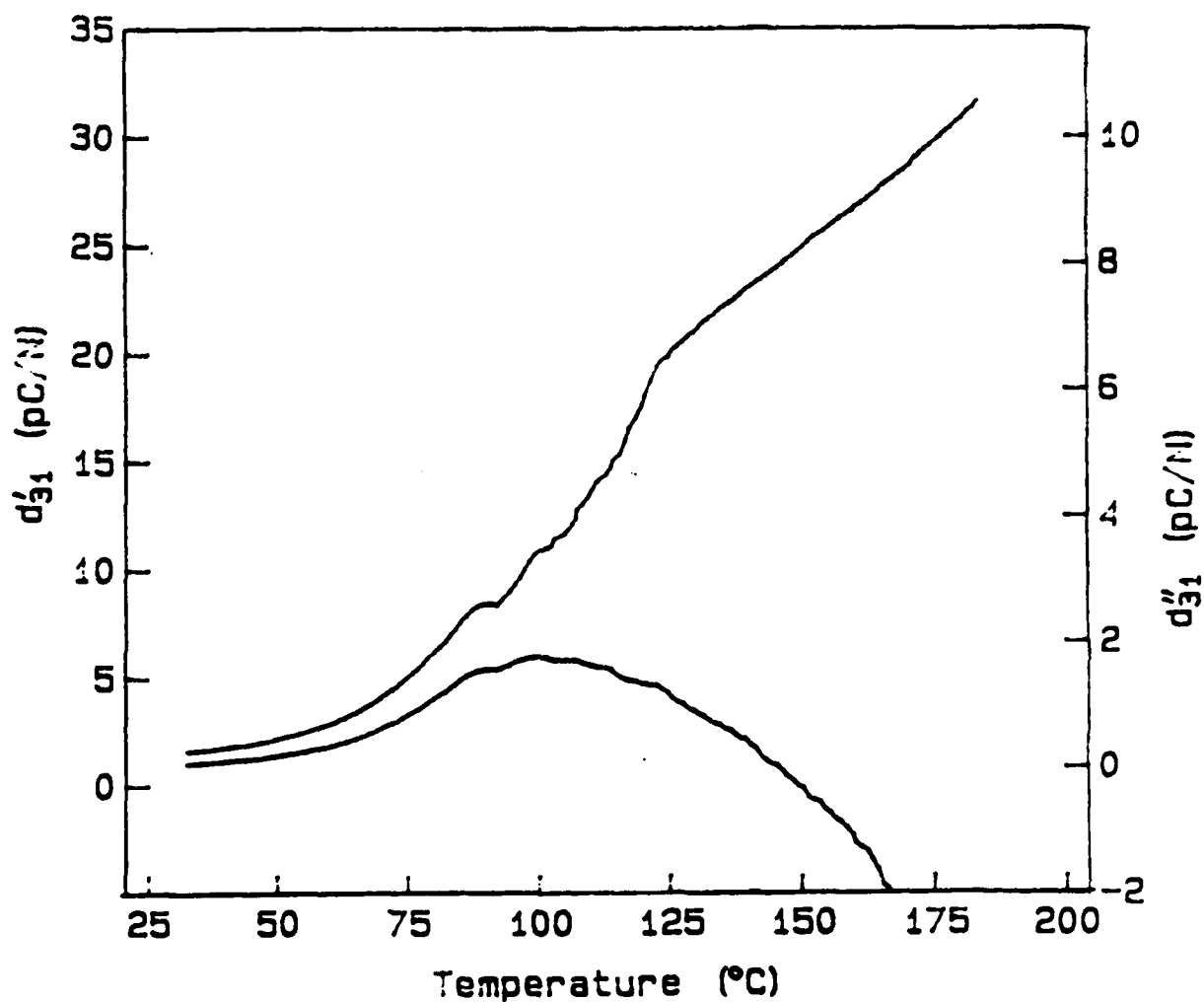
Temperature dependence of the piezoelectric stress constants, e_{31} , of Nylon 5.



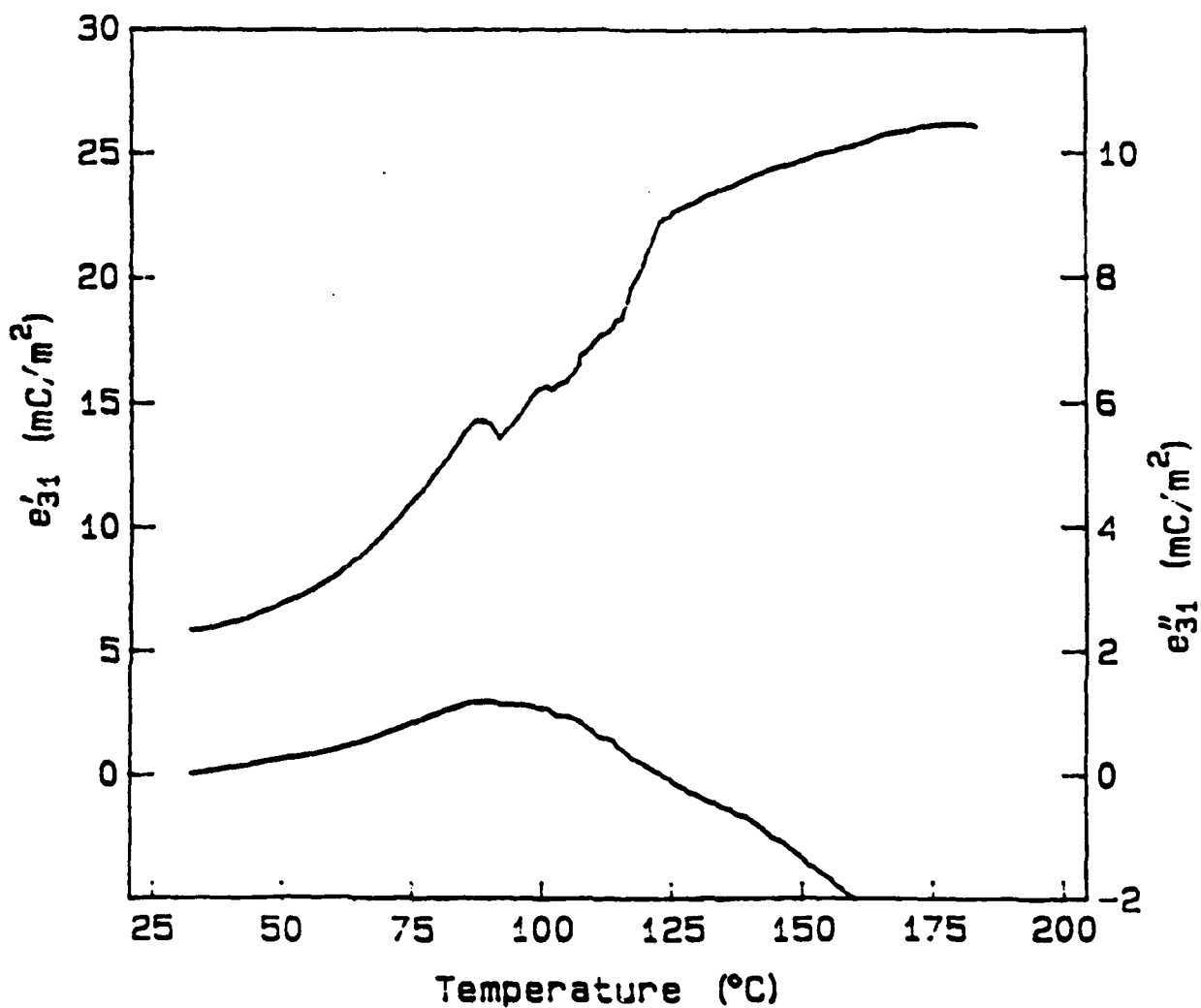
Current density versus electric field
for a) Nylon 11, b) Nylon 7, and c)
Nylon 11 / Nylon 7 blends (50%/50%)



D - E hysteresis loops of a) Nylon 11,
b) Nylon 7, and c) Nylon 11 / Nylon 7
blends (50%/50%)



Temperature dependence of the piezoelectric strain constants, d_{31} , of Nylon 11 / Nylon 7 blends (50%/50%).



Temperature dependence of the piezoelectric stress constants, e_{31} , of Nylon 11 / Nylon 7 blends (50%/50%).

UNIVERSITY OF SOUTHERN CALIFORNIA

Professor William P. Weber



COMPOSITE MATERIALS WITH IMPROVED PROPERTIES IN COMPRESSION



William P. Weber, Principal Investigator

II-G-3

Department of Chemistry
D.P. and K.B. Loker Hydrocarbon Research Institute
University of Southern California
Los Angeles, CA 90089-1661

DARPA/Office of Naval Research
Contract N00014-89-J-1961

SUMMARY:

- We will present results on a New Approach to Composite Materials with Improved Compressive Behavior in which we have taken advantage of unique Silicon-Carbon Chemistry.
- This is based on direct multi-site bonding of the polymeric matrix to the reinforcing fibers without the intervention of coupling agents. This will provide more direct integration of the fiber with the matrix and enhanced properties.
- Additionally, the remarkable properties (low dielectric constant and low moisture adsorption) of these matrix materials and their potential application for electronic packaging will be described.



Technology Transfer Agreement between the University of Southern California and Hercules, Inc.



- USC is actively pursuing patents on technology developed in Dr. Weber's laboratory. Hercules has obtained a two year exclusive option to study this technology as well as the first right to license it. We believe this agreement provides an excellent example of University-Industrial cooperation. It provides a viable mechanism to assure technology transfer.
- One patent application was filed in 1990, two were filed in 1991 and it is planned that an additional three patents will be filed in 1992.

II-G-5

Some of the information presented is Proprietary.

BACKGROUND

- Composite materials are made up of Matrix and Fiber.
- Failure generally occurs at the Matrix Fiber Interface.
- Coupling Agents are a partial solution to this problem.

For example, $(\text{EtO})_3\text{Si}-(\text{CH}_2)_3-\text{NH}_2$ significantly improves fiber glass reinforced epoxy laminates via chemical bonding. Siloxane (Si-O-Si) bonds are formed between the coupling agent and the surface silanol groups of the glass fiber while the amino functionality can form bonds with the epoxy network.

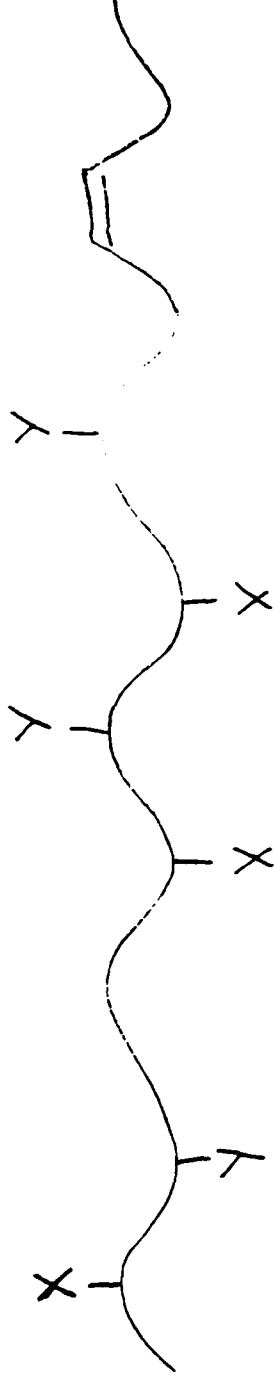
While composites have excellent properties in tension their properties in compression have been inadequate.

ON-GOING RESEARCH

Our goal has been to develop new types of Matrix Materials based on silicon-carbon chemistry with enhanced properties in compression. These will result from the novel bonding between Matrix and Fiber. These materials will be capable of the following:

1. Crosslinking to form a strong thermally stable network by well controlled chemistry.
2. Chemical bonding to the surface of reinforcing fibers by well controlled chemistry.
3. Low T_g and viscosity to facilitate coating of fibers (prepreg) and fine structures of microelectronic devices.
4. Retention of minimal elastomeric properties in crosslinked (cured) matrix material to prevent crack propagation and brittle fracture.

Schematic of Polymeric Matrix Material Before Curing



II-G-8

Polymeric Matrix Material before Cure

X = can bond to surface of fibers

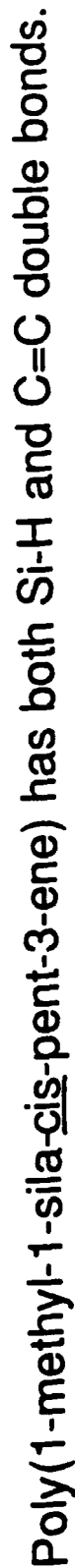
Y = can crosslink

cis C=C for elastomeric properties like cis-1,4-polybutadiene.

Fundamental Chemistry to be Utilized



Hydrosilation Reaction



These complementary functional groups are capable of crosslinking via Pt parts per million catalyzed hydrosilation reactions.

The Si-H groups are capable of Pt catalyzed reaction with surface silanol groups of glass fibers or surface hydroxy groups of oxidation activated carbon fibers.

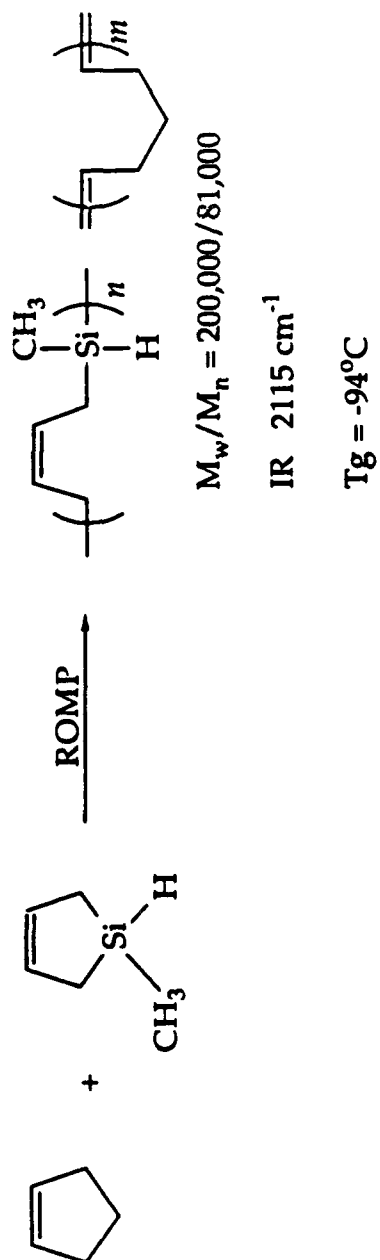
The monomer is readily available for inexpensive starting materials.

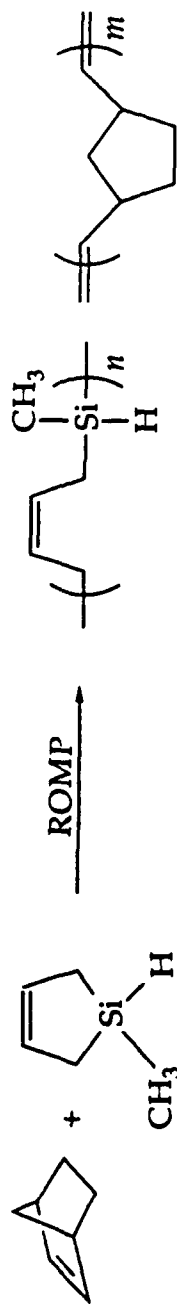
- We are currently preparing composite test samples made from poly(1-methyl-1-sila-cis-pent-3-ene) and unsized carbon fiber tow. Tests on these samples will be carried out during the Spring and early Summer of 1992 jointly with Hercules.

- A number of other unsaturated carbosilane polymer and copolymer systems have been prepared. Copolymers permit control of crosslink density and hence matrix rigidity.



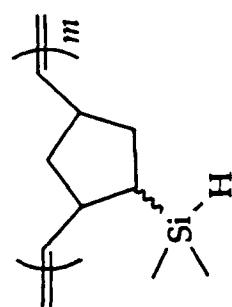




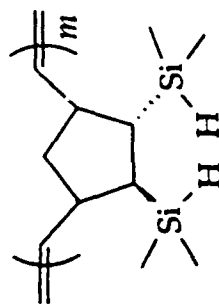
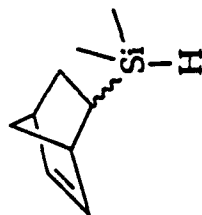


$M_w/M_n = 70,700/30,000$

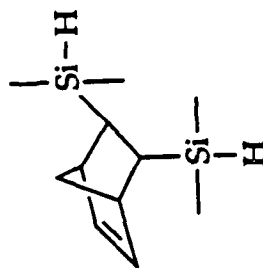
IR 2115 cm^{-1}



ROMP



ROMP



Development of Novel Low Dielectric Constant, Low Moisture Adsorbing Packaging Materials for Electronic Applications

Packaging has generally been a secondary consideration to silicon device fabrication in the design of microelectronic devices. This is changing since packaging **"limitations are beginning to impose restrictions on devices and system design"** as required for ultra high performance

18

L.T. Manzione, "Plastic Packaging of Microelectronic Devices," Van Nostrand Reinhold, New York, 1990, Chapter 1.

- Improved electronic packaging materials should have the following characteristics: Low Dielectric Constant since signal speed is inversely proportional to square root of the dielectric constant of the medium and low moisture adsorption since corrosion of aluminum connections depends on water.
- Current materials: epoxy and polyimides have problems in both these areas. The dielectric of both is about 4.2.
- Polypropylene (2.1), polyethylene (2.3) and Teflon (2.00-2.08) have low dielectric constants and low moisture adsorption. Coating electronic microstructures with them is difficult due to their high Tg's, and lack of crosslink chemistry.
- Crosslinking of our unsaturated carbosilane polymers via hydrosilation reaction yields a coating which has electrical properties like that of polypropylene.

but not as good as polypropylene

- We are in the Process of Identifying Packaging Demonstrations of Military Significance
- Interactions have been established at ETDL - Ft. Monmouth, New Jersey and at the Naval Research Laboratory, Washington, D.C.

UNIVERSITY OF SOUTHERN MISSISSIPPI

Professor Charles L. McCormick



THE UNIVERSITY OF SOUTHERN MISSISSIPPI

DEPARTMENT OF POLYMER SCIENCE

January 22, 1992

Dr. Richard Loda, DSO
DARPA
3701 North Fairfax Drive
Arlington, VA 22203-1714

Dear Rich:

I wish that I could say I feel good about our presentation at the DARPA meeting this past week. However, technical problems with the projection equipment destroyed many hours of preparation on our part.

On Tuesday, we were able to gather some valuable information from discussions with Charlie Stuart's group (Captain Charlie Young and Ed Carapezza) at DARPA and with Gene Remmers and Bill Martin at ONT as to the potential of polymers. Fortunately, our research descriptions and VCR tape of equipment and methods were enthusiastically received. Additional contacts and telephone conversations with the David Taylor Research Center, NRL, NUSC, and the Applied Physics Lab at Hopkins were made.

II-H-3

I have included a listing of four key accomplishments of our work. The first two should advance the technology of drag reduction in the kind of increments for which DARPA would hope. For the first time in 30 years of DR endeavor, a polymer can be designed and compared to the previous "best" in a logical way rather than in an Edisonian fashion. This can be done rapidly in the laboratory on a small scale prior to costly, and perhaps disastrous, scale-up and demonstration in the field. As you are well aware, all successful commercial products require at some time rapid, relatively inexpensive development studies on prototypes. We now have a device and a procedure to help with such developments in submarine, torpedo, or other technologies where drag reduction or turbulent suppression is important.

As I indicated to you, I will be on sabbatical leave (although still working on elements of DR) until July 1. My colleague, Roger Hester (601-266-4875) will be heading the research in my absence. He is also preparing some figures for you on fuel savings, load reduction, etc based on our determination of maximum DR effectiveness of an efficient and a less efficient polymer.

Remember, some of the information he needs for his calculations have not been forthcoming from the navy or DARPA and may require your assistance.

We realize you have a tough task in presenting the merits of your relevant projects to DARPA upper management. We trust that on close examination you will find significant accomplishments toward sound technological goals conducted in a scientifically competent manner at USM. We look forward to working further with you to meet our respective challenges in the months ahead.

Sincerely,

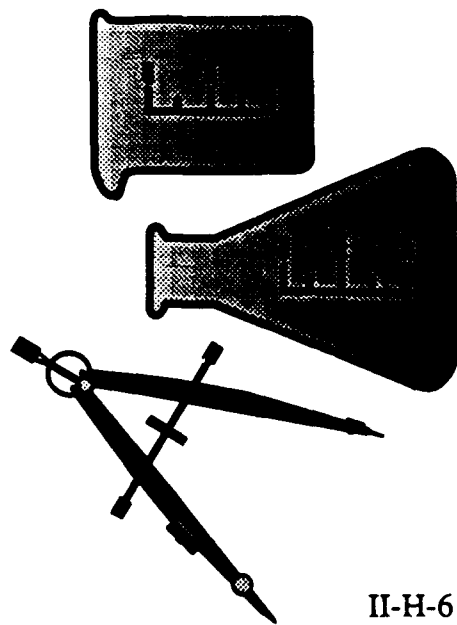
Charlie

Charles L. McCormick
Professor of Polymer Science

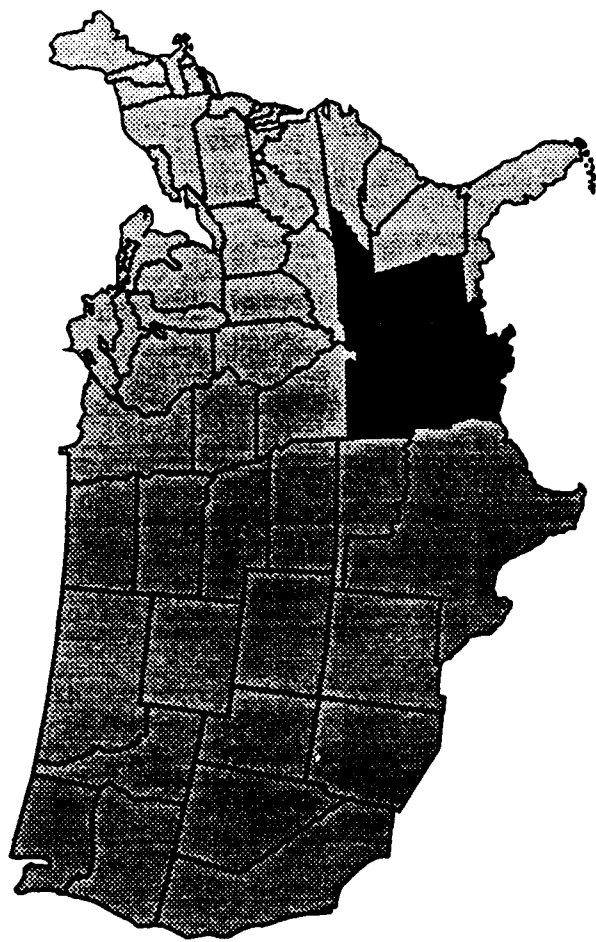
CLM/kmm

- Development of procedure which allows direct comparison and assessment of drag reduction performances of any experimental polymer systems
- Design and construction of an automated rotating disk apparatus to test drag reduction performance on laboratory scale polymers
- Molecular synthesis of polymers with enhanced drag reduction effectiveness (up to 10 times greater) as compared to PEO -- the standard polymer in past navy studies
- Design and construction of an acoustical interferometer for measuring water-polymer modes of energy dissipation

Effects of Polymer Structure and Solvation on Drag Reduction and Acoustic Behavior



II-H-6



**Charles L. McCormick
and Roger D. Hester**

**Polymer Science
University of Southern
Mississippi**



PRESENTATION OUTLINE



Introduction
Conceptual DR Models
Research Objectives
Target Synthetic Copolymers
Solvation/Association Characterization
DR Studies/Data Analysis
Empirical/Theoretical Relationships
Acoustic Interferometry
Accomplishments
Conclusions/Future Direction
Acknowledgements

Polymeric Drag Reduction

The ability of small concentrations of soluble high molecular weight polymer additives to reduce energy loss due to turbulent drag in high speed fluid flow.

PRESENTATION OUTLINE



Introduction
Conceptual DR Models
Research Objectives
Target Synthetic Copolymers
Solvation/Association Characterization
DR Studies/Data Analysis
Empirical/Theoretical Relationships
Acoustic Interferometry
Accomplishments
Conclusions/Future Direction
Acknowledgements

CLASSIFICATION OF DR MODELS

<u>Length based:</u>	Correlate with polymer chain length or radius of gyration.
<u>Time based:</u>	Scale with polymer relaxation time.
<u>Energy based:</u>	Depend on the ability of polymer molecules to alter the energy balance of the turbulent flow.

DRAG REDUCTION MODELS

VIRK'S MODEL: Virk related drag reduction effectiveness to polymer concentration, C in ppm, molecular weight, M, and degree of polymerization, N. He suggested that a plot of the reduced slope increment,

$$\Pi = \delta_r / (C/M)^{1/2} \quad \text{Equation 1}$$

as a function of degree of polymerization, N, should yield a straight line. δ_r is the slope increment for the polymer solution over the solvent in the Prandtl-von Karman plots.

RYSKIN'S MODEL: Ryskin recently developed a predictive theory based on his "yo-yo" model of polymer dynamics. He suggested the relationship,

$$[(\delta^2 + 4\delta)/2]^{1/2} = \alpha(aN[N_A C/2M]^{1/2}) \quad \text{Equation 2}$$

N_A = Avogadro's number
 a = length of repeat unit
 C = polymer concentration
 N = degree of polymerization

M = Molecular weight
 α = ratio of chain length to that
of a fully extended chain
 $\delta = \delta_r/2$

This relationship enables the experimental determination of α . Ryskin's analysis indicated that α should have a value of approximately 0.2.

WALSH'S MODEL: Walsh developed a model based on the energy storage capability of polymer and associated solvent. He defined a dimensionless parameter, H, which describes the effect of polymer additives on the rate of diffusion of turbulence near the wall. Onset of turbulence is predicted at $H = 0.01$ and maximum drag reduction at $H = 1$.

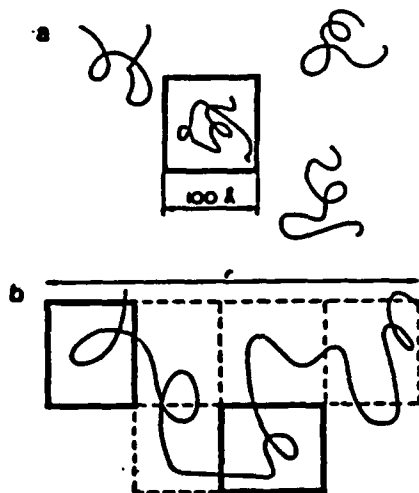
$$H = (8CM[\eta]^2\tau_w)/RT \quad \text{Equation 3}$$

C = polymer concentration
 $[\eta]$ = intrinsic viscosity
 τ_w = shear stress at the wall

M = molecular weight
 T = temperature
 R = gas constant

MOLECULAR AGGREGATION

HLAVACEK



Polymer molecules are not large enough to interfere with the turbulent eddies. Inter-molecular entanglements result in aggregates of greater size which could break up the eddies.

NEED FOR RESEARCH

- No Comprehensive, universally-accepted model for drag reduction exists
- The relationships between DR performance and macromolecular structure/solvation are not understood
- Tailored polymers with non-chain scission modes of energy dissipation need examination
- Interrelated effects of turbulence modification and acoustical modulation should be examined

Hypothesis

Copolymer structure and solvation
play an important role in drag
reduction.

Research Objectives

- Synthesize copolymers with Associative Interactions
- Design and Fabricate DR and Acoustic Instrumentation
- Elucidate Role of Water Structuring on DR Efficiency and Acoustic Modulation
- Correlate Empirical Relationship with Theoretical Models
- Establish Optimum Structural Features for DR and Turbulence Modification
- Optimize Photografting Procedure for Surface Modification

Handwritten signature

PRESENTATION OUTLINE

Introduction
Conceptual DR Models
Research Objectives
Target Synthetic Copolymers
Solvation/Association Characterization
DR Studies/Data Analysis
Empirical/Theoretical Relationships
Acoustic Interferometry
Accomplishments
Conclusions/Future Direction
Acknowledgements



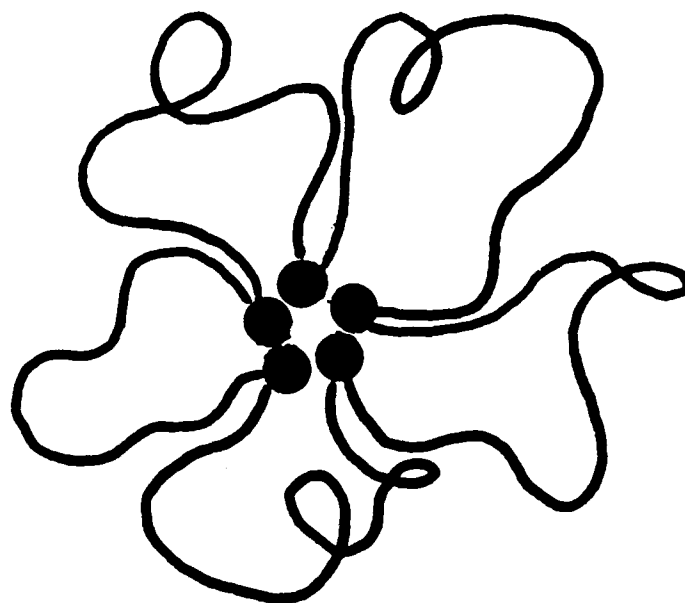
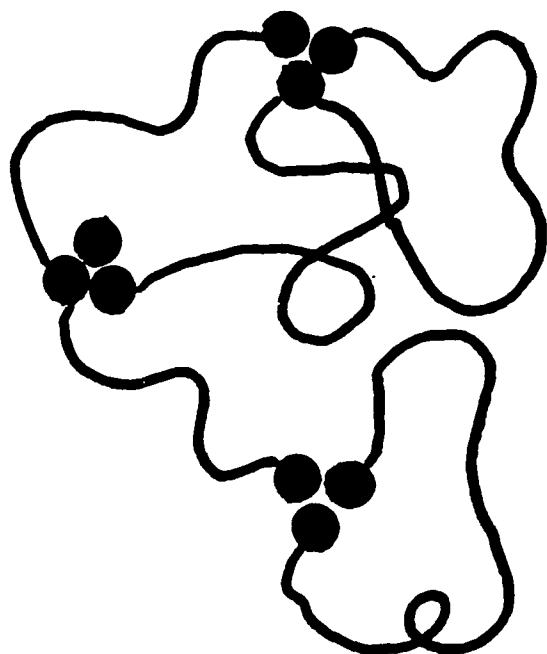
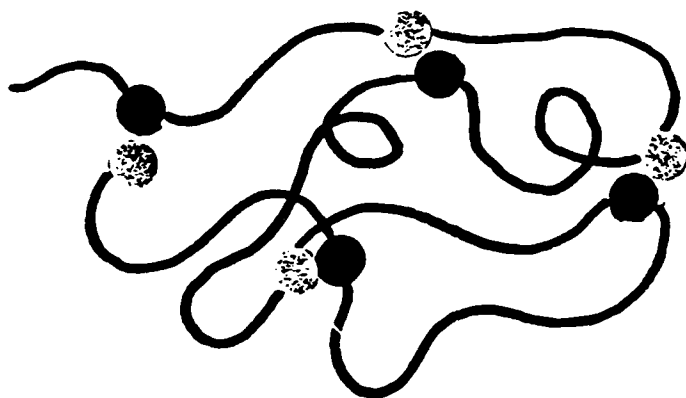
TARGET SYNTHETIC COPOLYMERS

Dissipative Modes of Energy Transfer
Potential for Maximal HDV Change

- Polyelectrolytes
- Ampholytes/Betaines
- Hydrophobic Domains
- Polymer/Surfactants
- Intramolecular H-Bonding

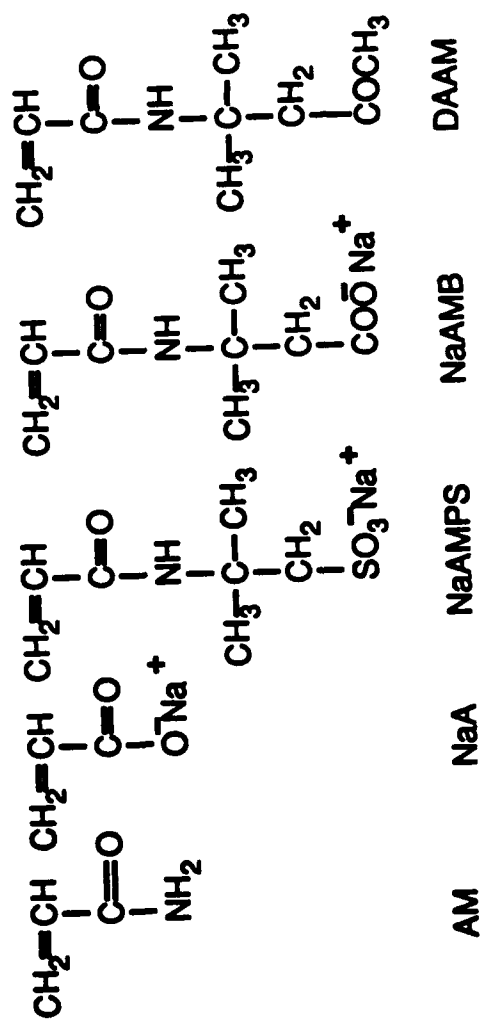


polymer

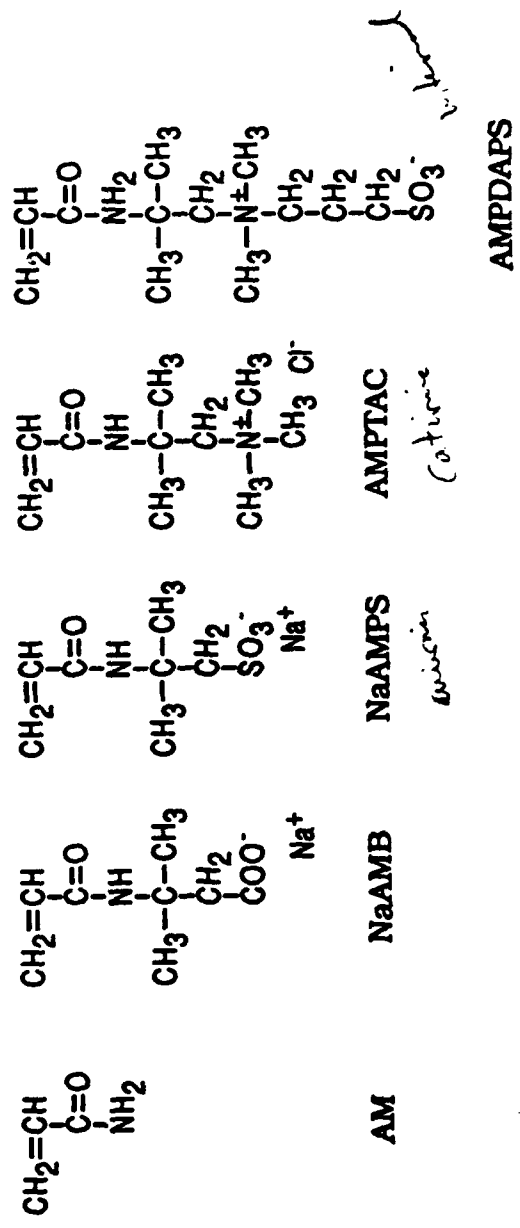


II-H-18

*polymer
hydroperoxide
associated - H₂O₂*



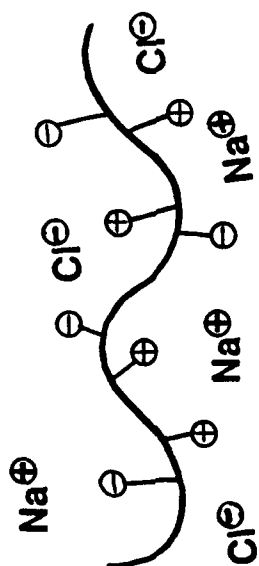
1-2
 2-2
 3-2
 4-2
 5-2
 6-2
 7-2
 8-2
 9-2
 10-2
 11-2
 12-2
 13-2
 14-2
 15-2
 16-2
 17-2
 18-2
 19-2
 20-2
 21-2
 22-2
 23-2
 24-2
 25-2
 26-2
 27-2
 28-2
 29-2
 30-2
 31-2
 32-2
 33-2
 34-2
 35-2
 36-2
 37-2
 38-2
 39-2
 40-2
 41-2
 42-2
 43-2
 44-2
 45-2
 46-2
 47-2
 48-2
 49-2
 50-2
 51-2
 52-2
 53-2
 54-2
 55-2
 56-2
 57-2
 58-2
 59-2
 60-2
 61-2
 62-2
 63-2
 64-2
 65-2
 66-2
 67-2
 68-2
 69-2
 70-2
 71-2
 72-2
 73-2
 74-2
 75-2
 76-2
 77-2
 78-2
 79-2
 80-2
 81-2
 82-2
 83-2
 84-2
 85-2
 86-2
 87-2
 88-2
 89-2
 90-2
 91-2
 92-2
 93-2
 94-2
 95-2
 96-2
 97-2
 98-2
 99-2
 100-2



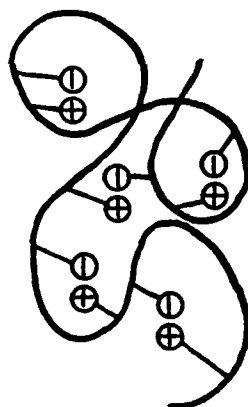
Nomenclature for the Polymer Series and Their Monomers

Series Name	AM	NaAMB	NaAMPS	AMPTAC	AMPDAPS
ABAM2	+	+	--	--	--
ATAM	+	--	--	+	--
ATAS	--	--	+	+	--
ATASAM	+	--	+	+	--
ATABAM	+	+	--	+	--
DAPSAM	+	--	--	--	+

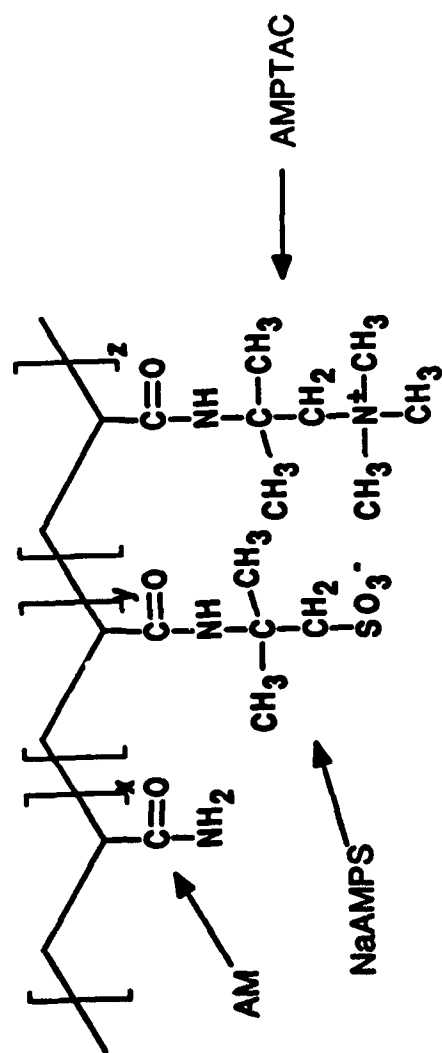
+ Monomer is incorporated in specified series.



Expanded
Chain



Compact
Chain



ATASAM TERPOLYMER

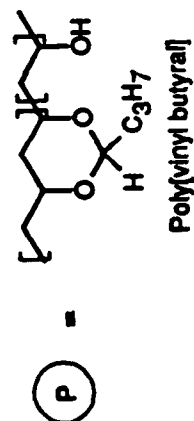
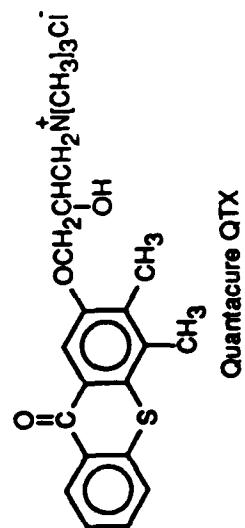
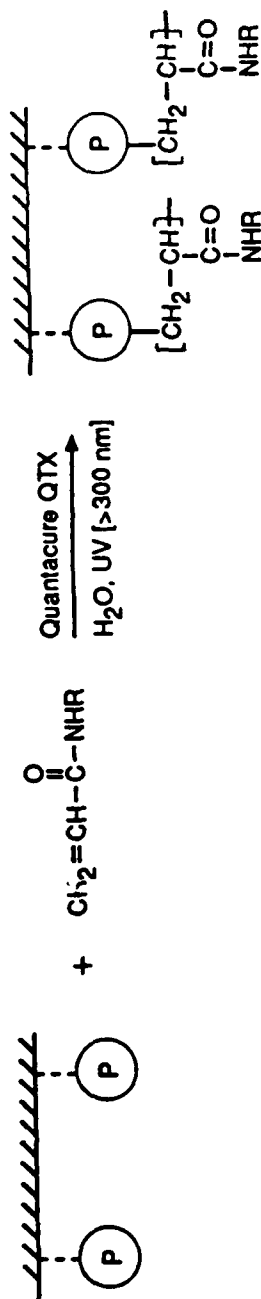
Classical and Quasielastic Light Scattering Data for Copolymers of Acrylamide (AM)
with 3-(2-Acrylamido-2-methylpropanedimethylammonio)-1-propanesulfonate (AMPDAPS)

Sample Number	AMPDAPS in Copolymer (mol %) ^a	dn/dc	Mw (x10 ⁻⁴ g/mol)	A ₂ (x10 ⁻⁴ ml·mol/g ²)	D ₀ x 10 ⁶ (cm ² /s)	d ₀ (Å)	DP x 10 ⁻⁴
DAPSAM-1	1 ^c	0.1450	3.2	2.67	5.05	1170	4.43
DAPSAM-5	5 ^c	0.1520	12.4	1.76	3.16	1650	15.1
DAPSAM-10-2	9.6	0.1385	7.0	1.49	4.01	1380	7.50
DAPSAM-10-3	10 ^b	0.1436	21.5	1.69	3.20	1530	23.0
DAPSAM-25-2	27.7	0.1395	8.2	1.33	3.97	1180	6.35
DAPSAM-40-2	38.9	0.1224	15.1	0.75	3.62	1420	9.57
DAPSAM-40-3	40 ^b	0.1546	17.5	1.21	3.24	1560	11.0
DAPSAM-60-2	58.8	0.1480	5.4	0.49	3.60	1430	2.71
DAPSAM-75-2	70.1	0.1293	6.2	0.48	4.90	1060	2.69
DAPSAM-100	100 ^c	0.1322	3.0	0.25	6.28	870	1.03

^a Determined from Elemental Analysis

^b Determined from ¹³C NMR

^c Theoretical



PRESENTATION OUTLINE

Introduction
Conceptual DR Models
Research Objectives
Target Synthetic Copolymers
Solvation/Association Characterization
DR Studies/Data Analysis
Empirical/Theoretical Relationships
Acoustic Interferometry
Accomplishments
Conclusions/Future Direction
Acknowledgements

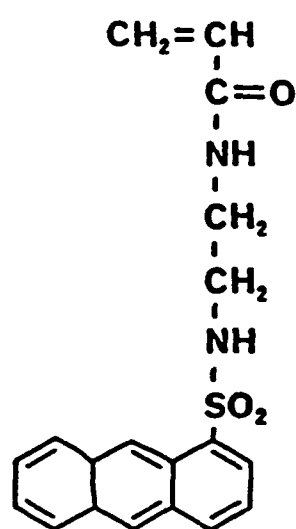
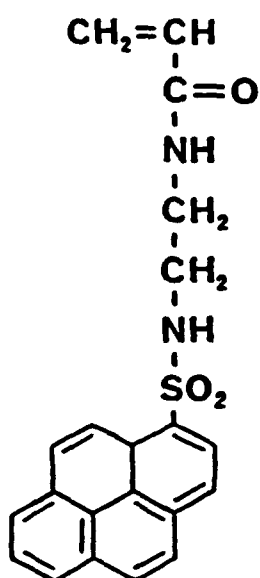
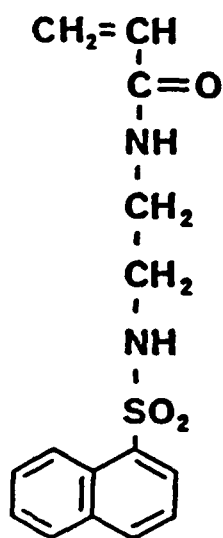


II-H-25

Associative Interactions

- Photophysical Studies
 - Labels/Probes
 - Excimer/Monomer
 - Fluorescence Lifetime
 - Fluorescence Quenching
- NMR/ESR Spin Probes
- MRI Studies *Magnetic Resonance Imaging*
- Environmental SEM

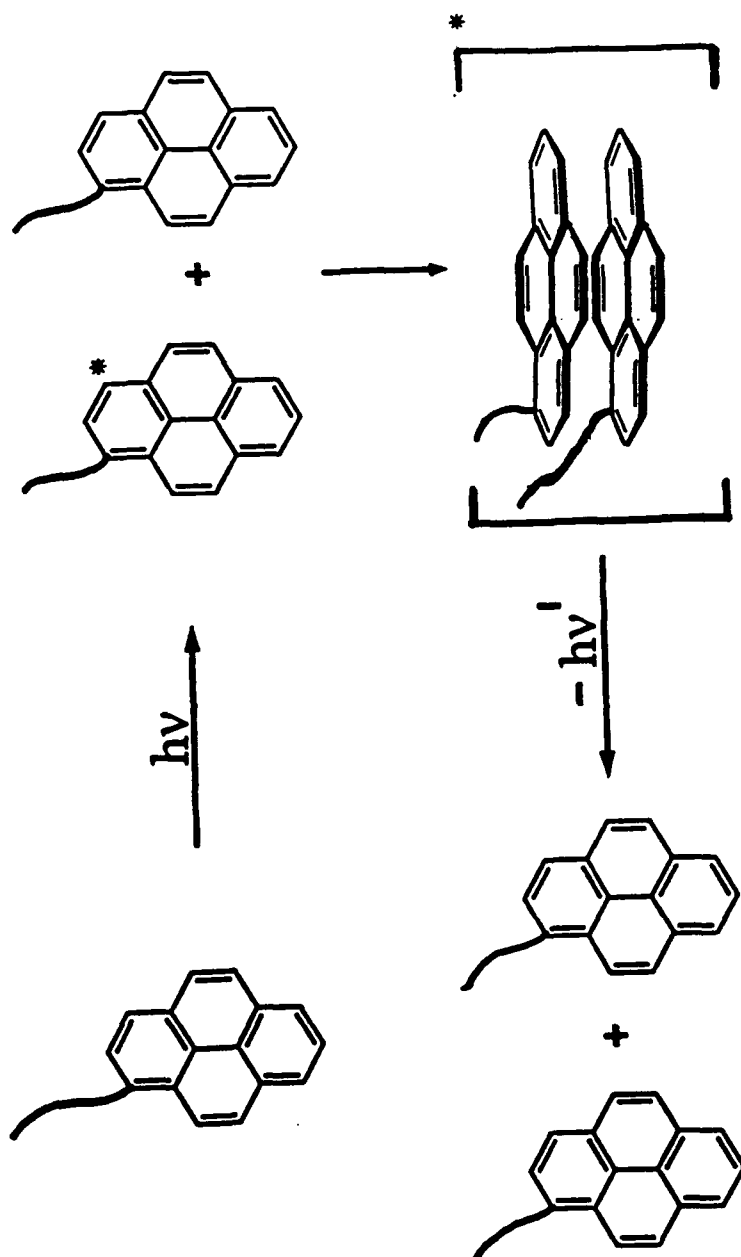
Fluorescent Monomer Probes

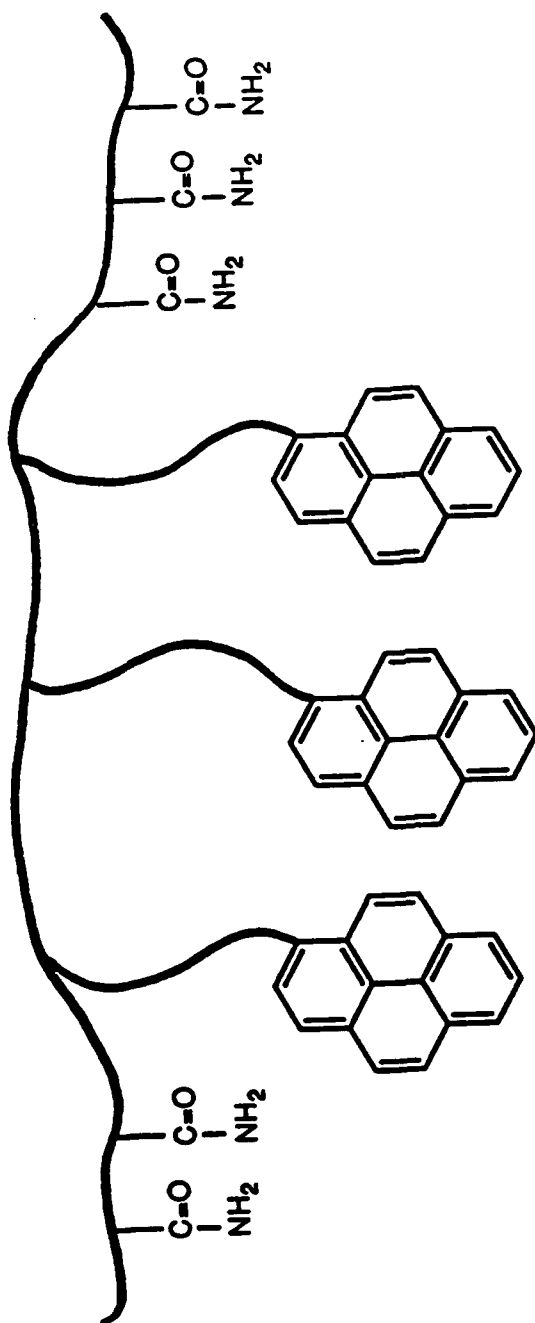


↑
model
for
hydrophobic
monomer.

Surfactant
polymerization kinetics.

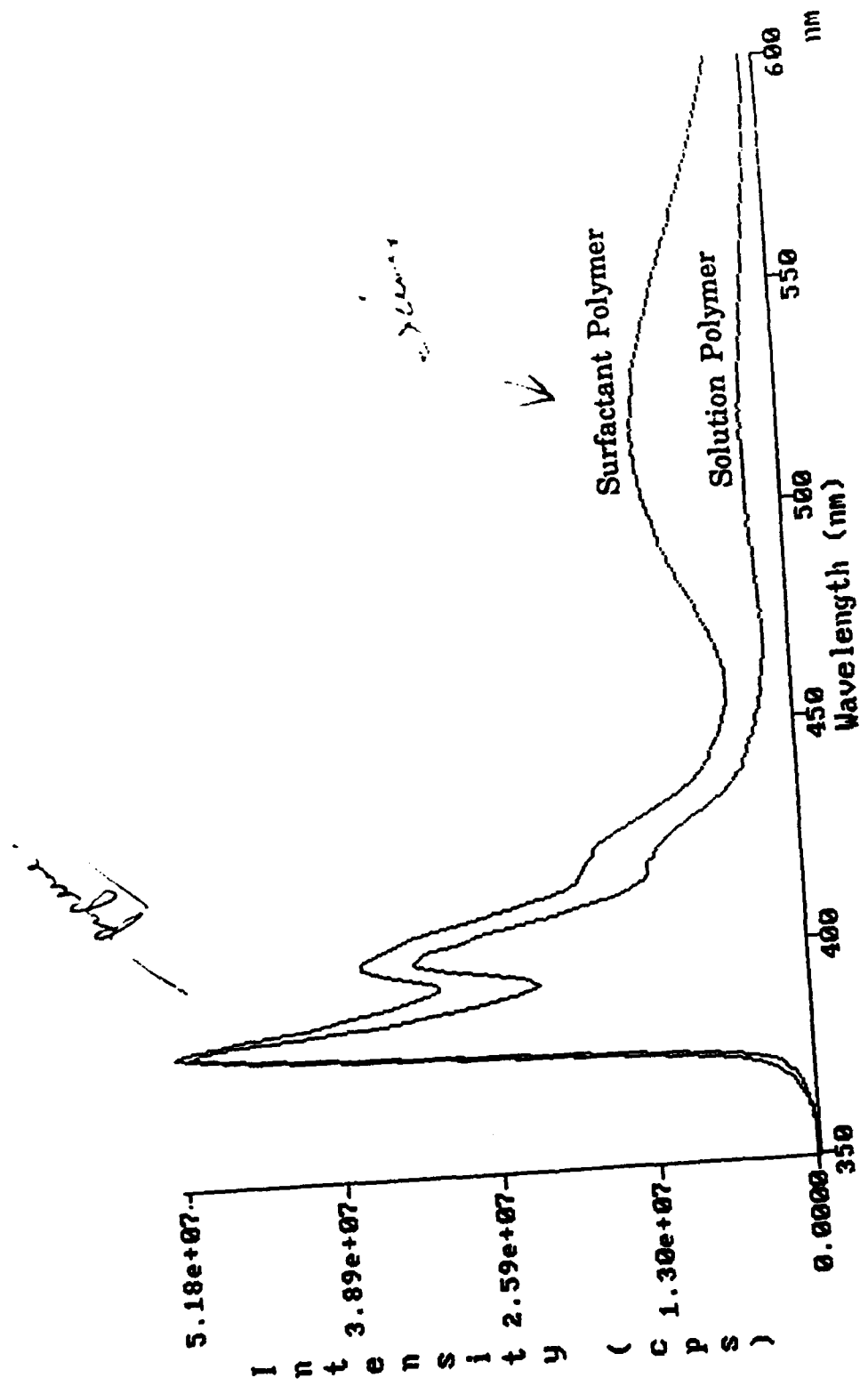
Excimer Emission





Surfactant-Polymerized AM-APS

... de surface de l'interface

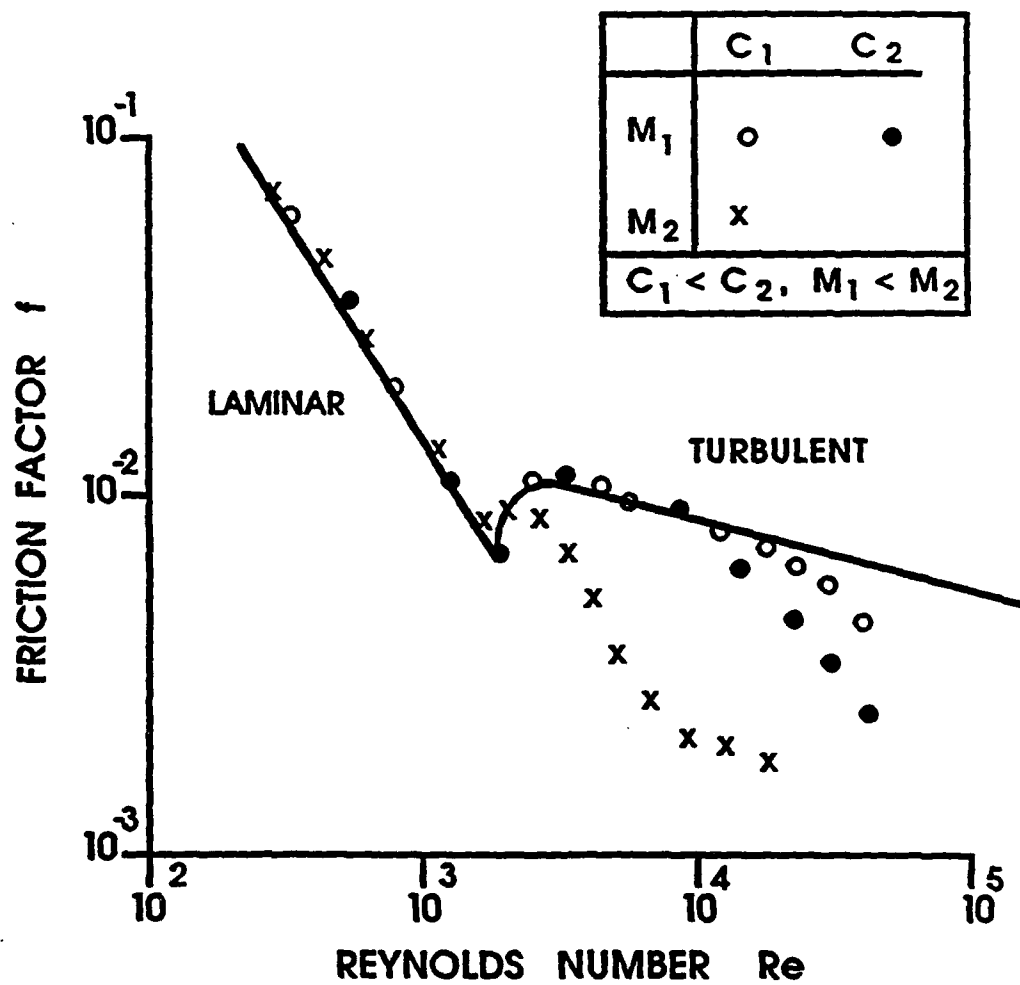


PRESENTATION OUTLINE

Introduction
Conceptual DR Models
Research Objectives
Target Synthetic Copolymers
Solvation/Association Characterization
DR Studies/Data Analysis
Empirical/Theoretical Relationships
Acoustic Interferometry
Accomplishments
Conclusions/Future Direction
Acknowledgements



II-H-31



$$\% \text{ DR} = 100 \times (f_s - f_p) / f_s$$

DR Shift Factors

Polymer	Shift Factors in Disk Flow
<i>Homopolymers:</i>	
PEO WSR-301	1.0
PAM-4	2.0
<i>Copolymers:</i>	
DAAM 15	1.3
DAAM 20	2.2
DAAM 25	6.5
DAAM 30	8.0
DAAM 35	10.0
NaA 5	3.0
NaA 10	3.0
NaA 20	8.0
NaA 35	0.35
NaAMB 5	3.5
NaAMB 10	3.5
NaAMB 25	3.5
NaAMB 40	3.5
NaAMB 100	0.075
NaAMPS 5	2.1
NaAMPS 10	2.1
NaAMPS 15	2.1
NaAMPS 20	2.1
NaAMPS 35	2.1
NaAMPS 100	0.09

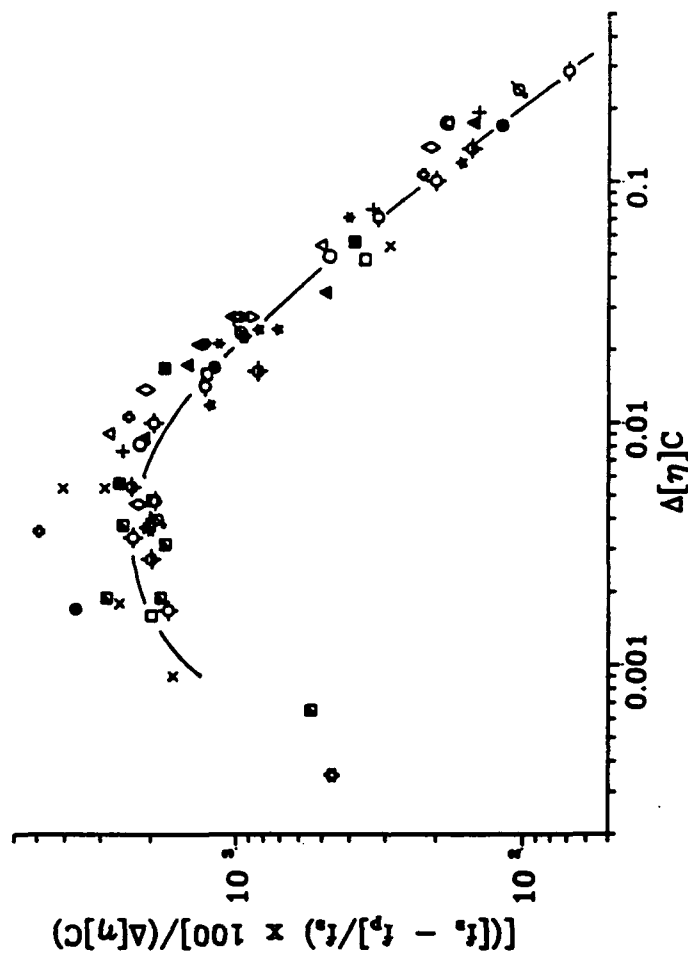


Figure 6: Drag reduction efficiency vs polymer volume fraction employing shift factors for polymer solutions in disk flow at $Re = 520,000$; PEO-WSR 301 (\square), PAM-4 (\cdot), DAAM 15 (\times), DAAM 20 (\diamond), DAAM 25 ($+$), DAAM 35 (ϕ), NaAMPS 5 (\ominus), NaAMPS 10 (\circ), NaAMPS 15 (\oplus), NaAMPS 20 (ϕ), NaAMPS 35 (\ominus), NaAMB 5 ($+$), NaAMB 10 (\ominus), NaAMB 25 (Δ), NaAMB 100 (\boxtimes), NaA 10 (∇), NaA 35 (\oplus).

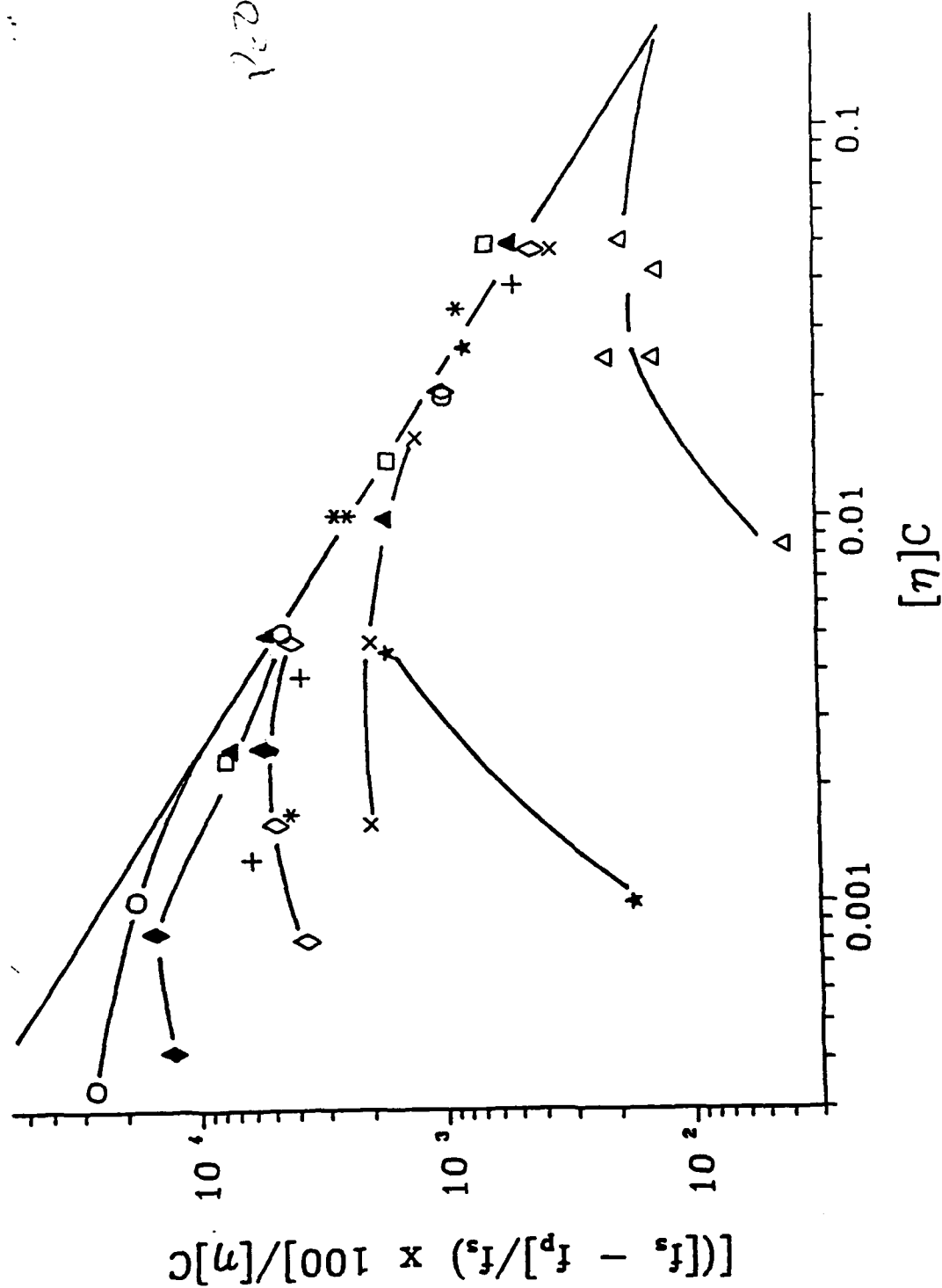
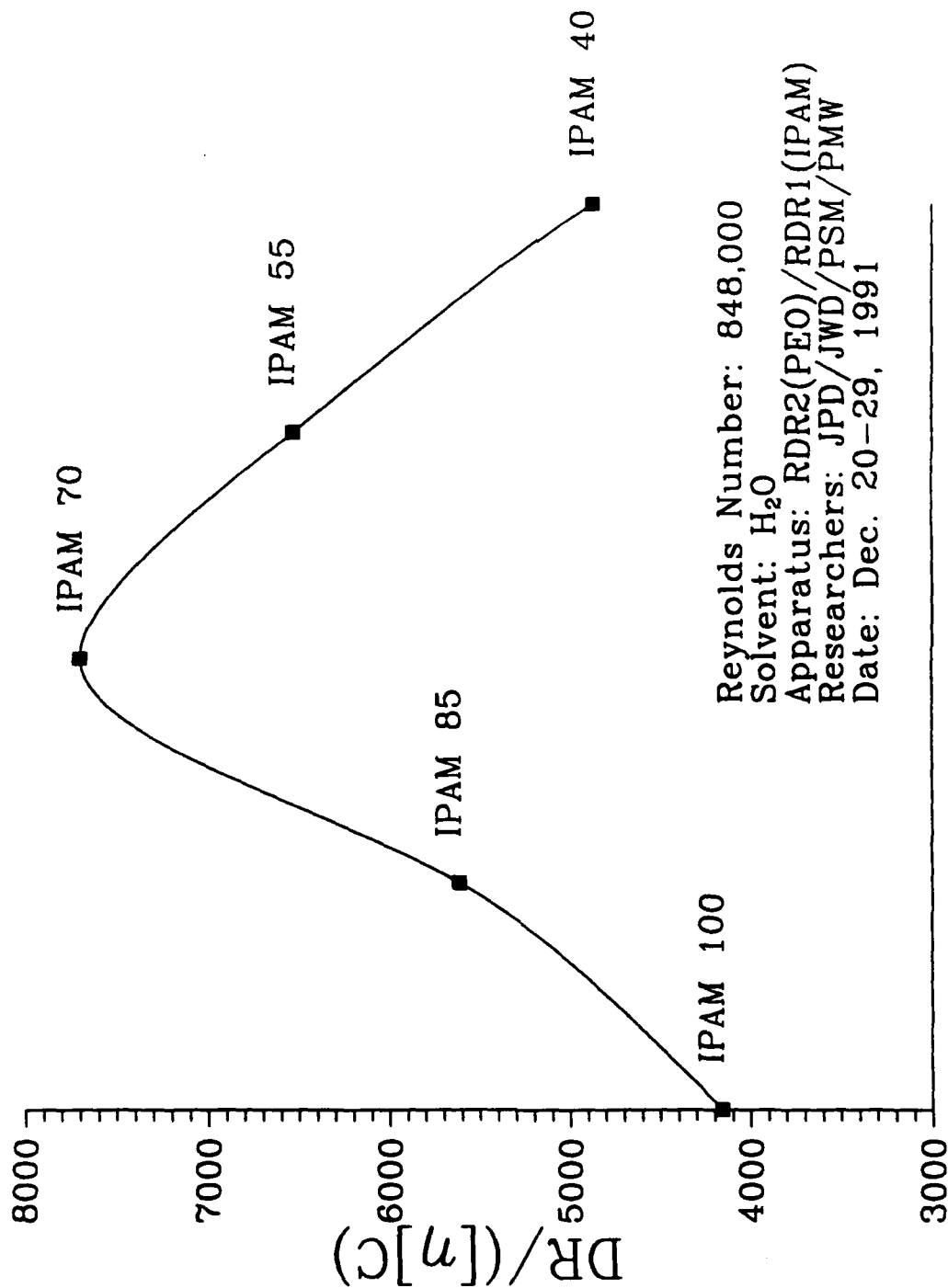


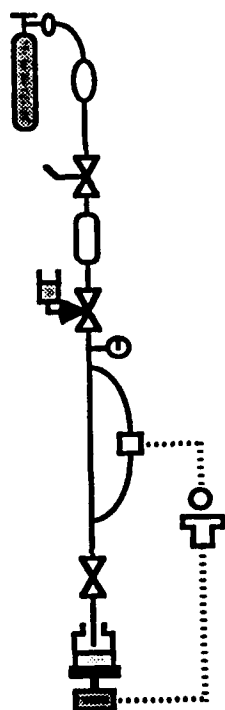
Figure 5: Drag reduction efficiency as a function of polymer volume fraction in 0.514 M NaCl solutions in disk flow at $Re = 520,000$; PEO-WSR 301 (\times), PAM-4 (*), DAAM 20 (\diamond), DAAM 25 (\diamond), DAAM 35 (O), NaA 5 (+), NaA 10 (\square), NaA 35 (\star), NaA 100 (Δ), NaAMB 40 (Δ).

EFFICIENCY PLOT Efficiency at $[\eta]_c = 0.002$



Reynolds Number: 848,000
Solvent: H₂O
Apparatus: RDR2(PEO)/RDR1(IPAM)
Researchers: JPD/JWD/PSM/PMW
Date: Dec. 20-29, 1991

TUBE FLOW DRAG REDUCTION MEASUREMENTS



HIGH PRESSURE NITROGEN
SOURCE WITH REGULATOR
CONSTANT PRESSURE RESERVOIR

3-WAY BALL VALVE (WHITEY)
WITH PURGE VALVE

SAMPLE RESERVOIR (1000 CC)

3-WAY BALL VALVE FOR SAMPLE
LOADING
PRESSURE GAUGE

SS CAPILLARY TUBE
(0.210 CM X 100 CM)
DIFFERENTIAL PRESSURE
TRANSDUCER (VALIDYNE DP15-48)

DIGITAL MULTIMETER

RECORDER (HP 7040A)

SHUT - OFF VALVE

SAMPLE COLLECTION

1000 GM LOAD CELL (SHAEVITZ)

$$f = \frac{\pi^2 D^5 \Delta P}{32 L \rho Q^2}$$

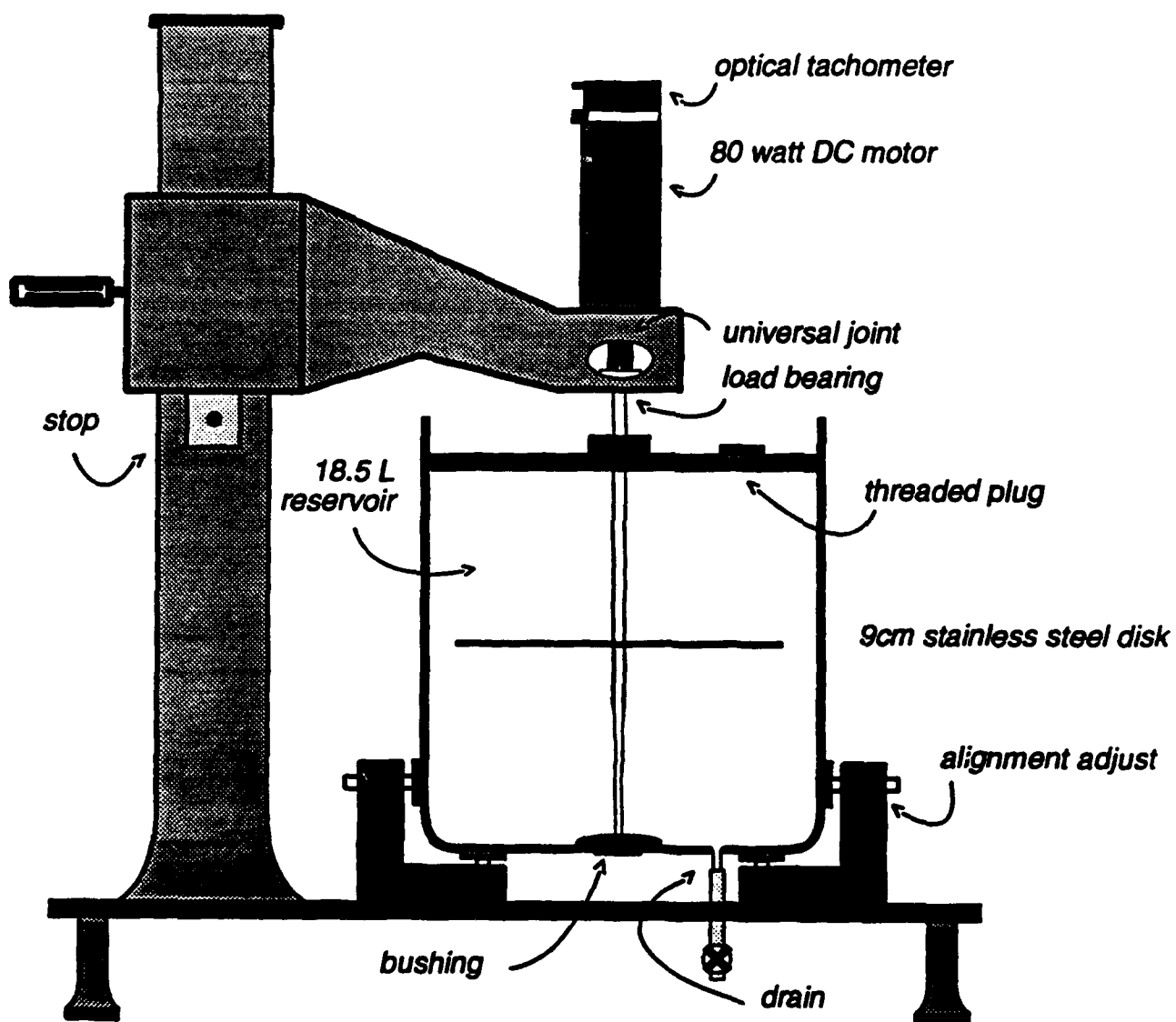
$$Re = \frac{4 \rho Q}{\pi D \mu}$$

Rotating Disk Rheometer

- Large volume
- Well defined geometry
- Easy variation of Re
- Large range of Re obtained
- Only small portion of solution in turbulent flow
- Disk surface can be modified or coated
- Larger mass of polymer needed

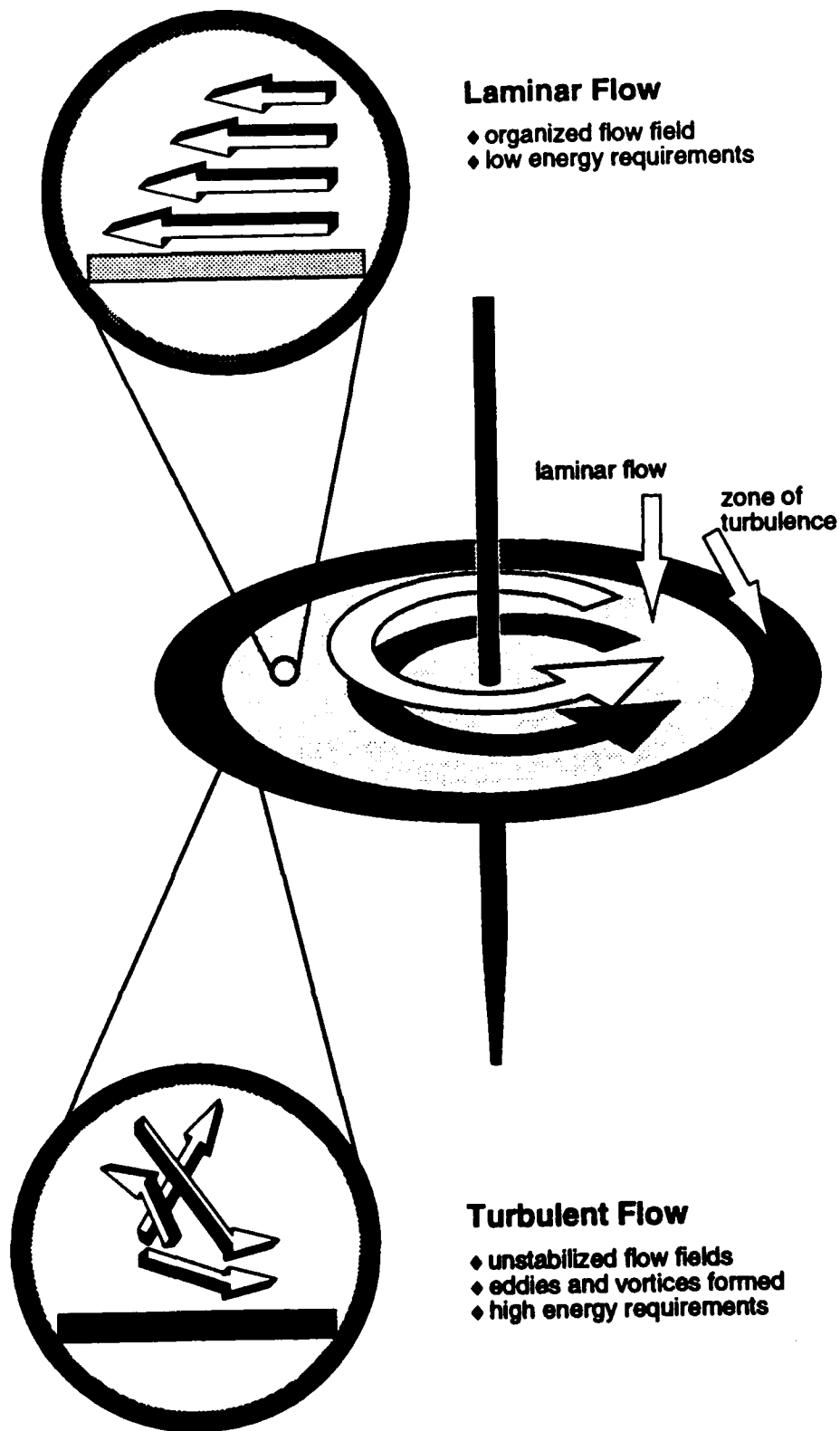
$$Re = \frac{2\pi \cdot N \cdot \rho \cdot R^2}{\mu}$$

ROTATING DISK RHEOMETER



II-H-38

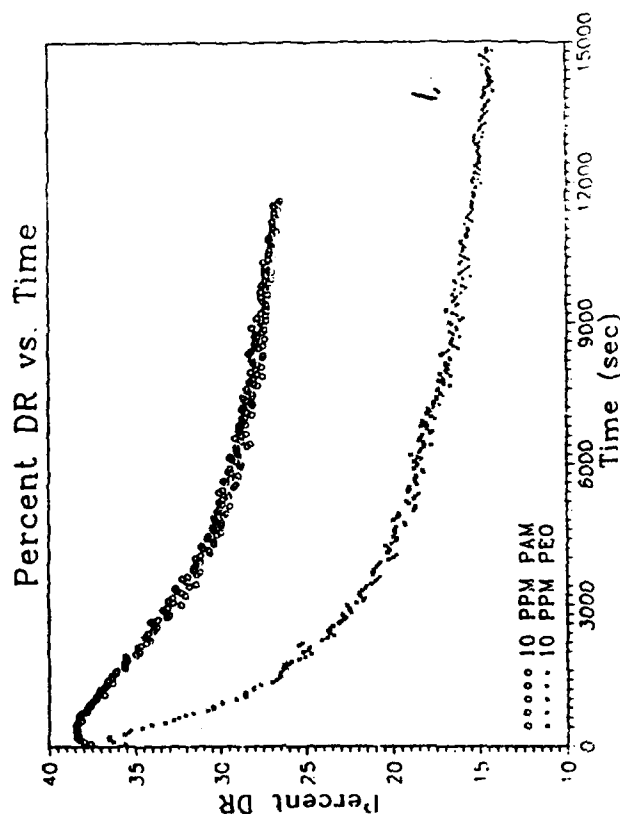
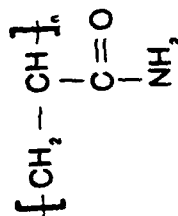
Disk Surface Flow Fields



Poly(acrylamide) - PAM

- Low shear degradation
- Has good DR properties
- Mark-Houwink parameters established

Source: American Cyanamide Magnifloc 900N



new stable
the

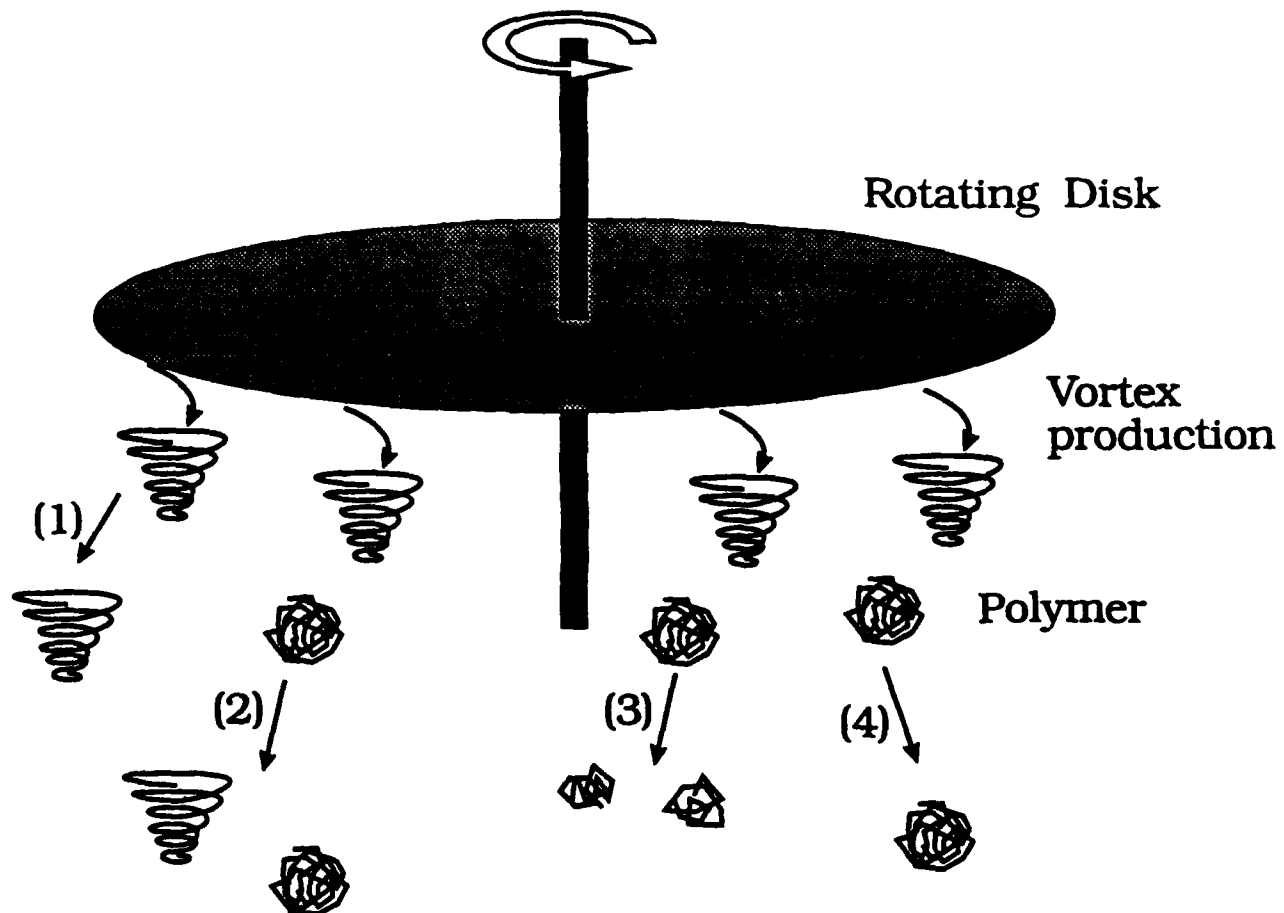
DR degradation

PRESENTATION OUTLINE

Introduction
Conceptual DR Models
Research Objectives
Target Synthetic Copolymers
Solvation/Association Characterization
DR Studies/Data Analysis
Empirical/Theoretical Relationships
Acoustic Interferometry
Accomplishments
Conclusions/Future Direction
Acknowledgements



Drag Reduction Mechanism Hypothesis



- 1) No collision between polymer and vortex.
Vortex unaltered and exits the boundary layer.
- 2) Collision between polymer and vortex without alteration of vortex or polymer.
- 3) Collision between polymer and vortex with vortex destruction and polymer degradation.
- 4) Collision between polymer and vortex with vortex destruction and no polymer degradation.

Drag Reduction Mechanism Formalization

V	Volume fraction of "live" microvortices	$[\eta]$	intrinsic viscosity
D	"dead" microvortices	c	polymer concentration
P	Polymer fraction	k	rate constant
		t	time.

Rate Equations

Vortex Birth



$\rightarrow V$

$$\left(\frac{dV}{dt} \right)_1 = k_b$$

*live
vortex
k_b*

"Natural" Vortex Death

$V \rightarrow D$

$$\left(\frac{dV}{dt} \right)_2 = -k_n \cdot V$$

Vortex "Death" by Polymer

$V + P \rightarrow D + P$

$$\left(\frac{dV}{dt} \right)_3 = -k_p \cdot V \cdot P = -k_p \cdot V \cdot [\eta]c$$

Steady State Conditions

$$\left(\frac{dV}{dt} \right)_1 + \left(\frac{dV}{dt} \right)_2 + \left(\frac{dV}{dt} \right)_3 = 0$$

$$k_n \cdot V + k_p \cdot V [\eta]c = k_b \quad \rightarrow \quad V = \frac{k_b}{k_n + k_p \cdot [\eta]c}$$

- Solution Drag (D_s) is assumed to be proportional to the Volume Fraction of "Live" microvortices (V).

$$D_s = k \cdot V \quad \text{thus} \quad D_s = \frac{1}{k} \cdot \frac{k_b}{k_n + k_p \cdot [\eta]c}$$

- For solvent only, $c = 0$, and the solvent drag (D_0) is:

$$D_0 = \frac{1}{k} \cdot \frac{k_b}{k_n}$$

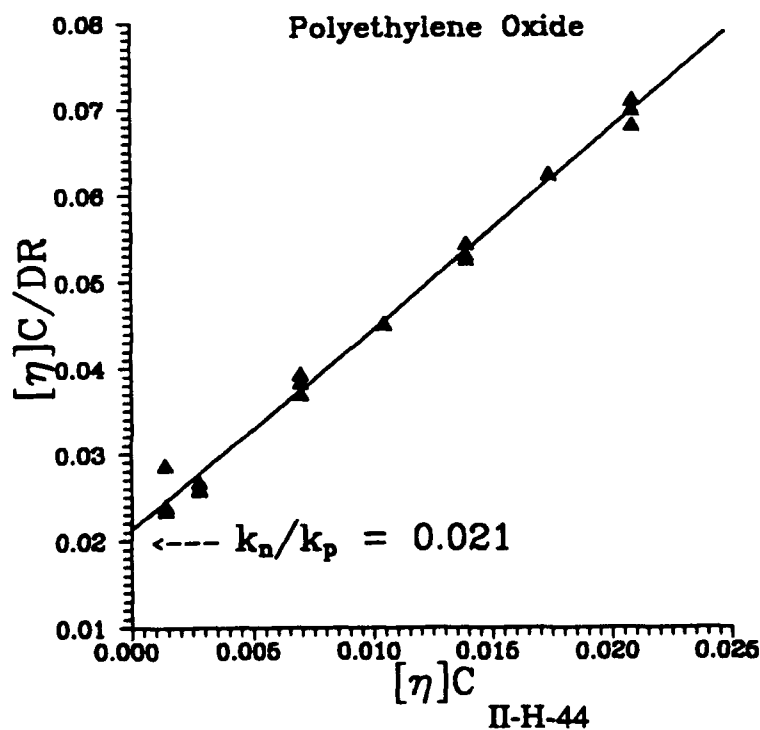
- Drag Reduction (DR) definition:

$$DR = 1 - \frac{D_s}{D_0} = 1 - \frac{k_n}{k_n + k_p \cdot [\eta]c}$$

- Rearrangement to a linear form gives:

$$\frac{[\eta]c}{DR} = \frac{k_n}{k_p} + [\eta]c$$

- Typical Plot of Data



intercept = 0.021

Model Summary

Polymer	Rate Constant Ratio ($\frac{k_n}{k_p}$)	Ratio to PEO Standard(Δ)
PEO (WSR-N-60K)	0.021	1.00
PAM (900N)	0.013	1.65
IPAM-100	0.020	1.09
IPAM-85	0.014	1.52
IPAM-70	0.009	2.24
IPAM-55	0.012	1.78
IPAM-40	0.017	1.29
DAAM-35	-----	10.0

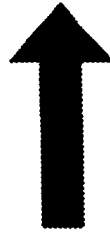
(all polymers were run in DI H₂O using a rotating disk rheometer at $N_{Re} = 848,000$, except DAAM-35 at $N_{Re} = 520,000$ in 0.514M NaCl)

- The above analysis indicates that Δ is a measure of polymer structure effectiveness in decreasing the number of microvortices when compared to the performance of the PEO standard.
- Delta is related to:
 - ? polymer coil deformations
 - ? changes in solvent-polymer interactions
 - ? disruptions of intra-polymer associations

PRESENTATION OUTLINE

Introduction
Conceptual DR Models
Research Objectives
Target Synthetic Copolymers
Solvation/Association Characterization
DR Studies/Data Analysis
Empirical/Theoretical Relationships
Acoustic Interferometry
Accomplishments
Conclusions/Future Direction
Acknowledgements

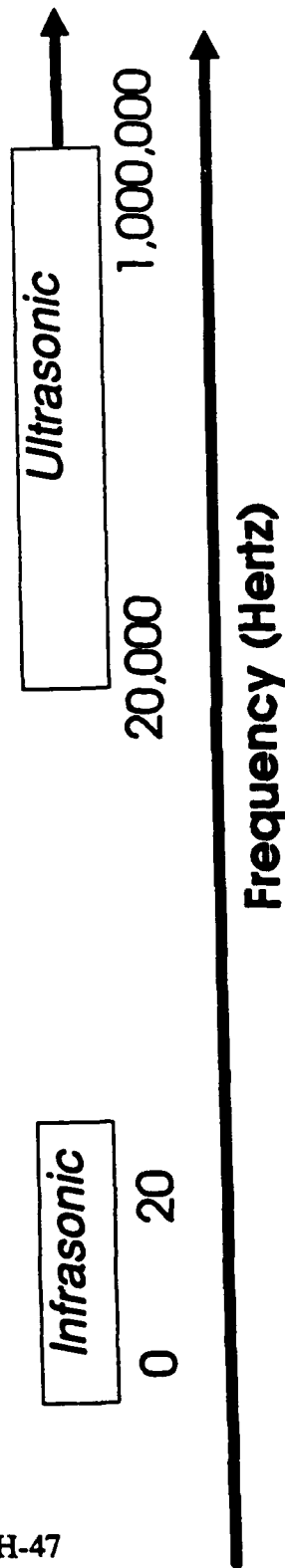
II-H-46



Acoustic spectra

Acoustics - The generation, transmission, and reception of energy in the form of vibration waves in matter.

II-H-47



Acoustical Attenuation

Attenuation increases as frequency squared; therefore, most times it is plotted as $\frac{\alpha}{f^2}$ and deviations from a horizontal line are noted.

$$\frac{\alpha}{f^2} = B + \sum_{i=1}^n \frac{A_i}{1 + \left(\frac{f}{f_{ci}}\right)^2}$$

Structural Change

$$B = \frac{2\pi^2}{\rho C^3} \left\{ \frac{4}{3} \eta_s + \eta_v + \frac{K}{C_p} (\gamma - 1) \right\} + \frac{\alpha}{f_{vb}^2}$$

Viscous
Effects

Thermal
Effects

Vibrational
Effects

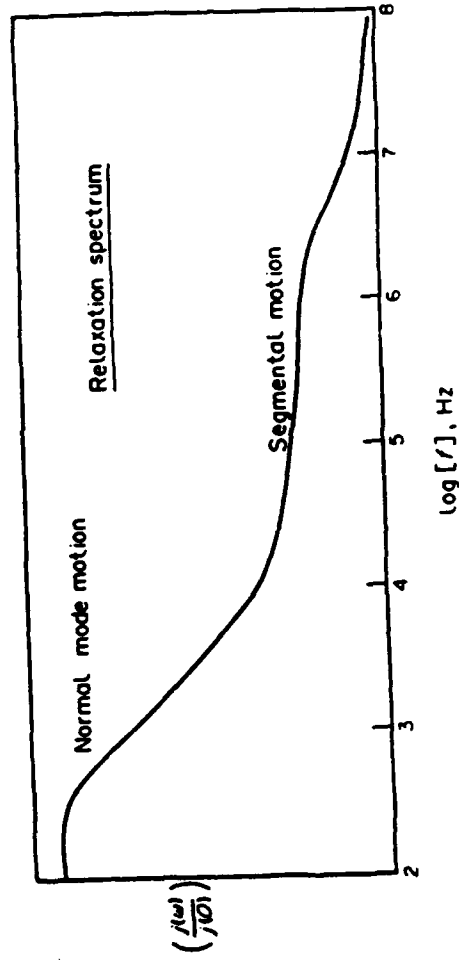
Relaxation Spectrum

Region 1 (low frequency)

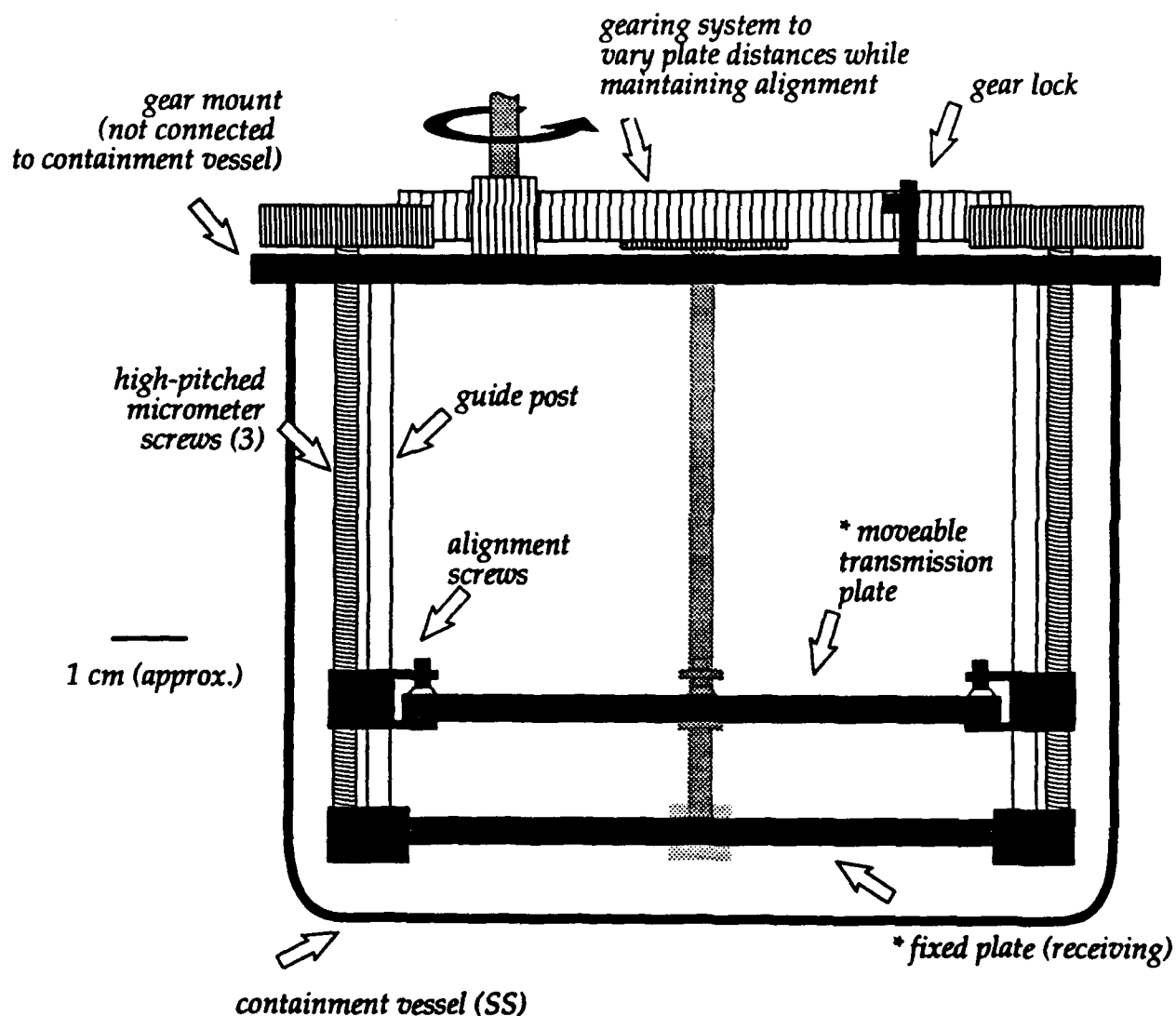
- Normal mode relaxation processes
- Relatively insensitive to solvent conditions

Region 2 (high frequency)

- Segmental mode relaxation processes
- Shifts occur due to solvent conditions



Design for High Thermal Stability Acoustic Interferometer Cell



* The two quartz plates are easily replaceable giving the ability to use plates holding crystals of several different fundamental resonances.

Summary

Build an acoustic interferometer capable of both static and turbulent measurements.

Probe molecular level relaxation events using acoustical attenuation.

Examine the polymer/solvent structure using acoustical velocity measurements.

Relate these acoustic measurements to proposed drag reduction mechanisms.

Questions

How does turbulent flow effect relaxation events? How do these relate to chemical composition?

Does the compressibility of the polymer/solvent system relate to the drag reduction efficiency and if so, is it a hydrodynamic effect or something else?

Does the solvation shell around the polymer backbone enhance energy transfer from solvent to polymer, and vice versa?

PRESENTATION OUTLINE

Introduction
Conceptual DR Models
Research Objectives
Target Synthetic Copolymers
Solvation/Association Characterization
DR Studies/Data Analysis
Empirical/Theoretical Relationships
Acoustic Interferometry
Accomplishments
Conclusions/Future Direction
Acknowledgements



Accomplishments

**Target Copolymer Synthesis
Macromolecular Characterization
Fluorescence Studies
Rheological Characterization
Rotating Disk Instrumentation
Tube Flow Apparatus
DR Efficiency Measurement
Empirical/Theoretical Relationships
Photografting onto Disks
Acoustic Interferometer**

Acknowledgements

DARPA/ONR

MS/AL Sea Grant Consortium

Dr. Sara Morgan Goff

Mark Clark

John Middleton

Steve Ezzell

Abbas Safieddine

General Electric

Eastman Kodak

Monsanto

3-M

General Electric

Luis Salazar

Yihua Chang

Kent Newman

Pavneet Mumick

Mark Logan

Mark Kramer

Erich Kathmann

Kelly Branham

James Dickerson

Mike Flesher

Stuart Hartfield

HOECHST CELANESE RESEARCH DIVISION

Dr. Morton M. Glick

POLYMER BLENDS
DARPA ORDER NO. 6045
AFOSR NO. F49620-88-C-0014

FINAL REPORT
DR. MORTON M. GLICK
JANUARY 15, 1992

HOECHST CELANESE RESEARCH DIVISION
SUMMIT, NEW JERSEY

POLYMER BLENDS TEAM
PRINCIPAL INVESTIGATOR - M. JAFFE

MATERIALS

HOECHST CELANESE
E. CHENEVEY
W. COOPER
M. GLICK
I. HAIDER

AEROSPACE

LOCKHEED
R. BOSCHAN
G.E. ENGINES
R. GRIFFIN

UNIVERSITY

UMASS
F. KARASZ
W. MACKNIGHT
V.P.I.
J. MCGRATH

POLYMER BLENDS

BACKGROUND - UMASS PROGRAM - 1984-1987

**. IDENTIFY POLYMER BLENDS MEETING AEROSPACE
HIGH TEMPERATURE REQUIREMENTS**

**PBI/PI FEASIBILITY AS HIGH T MATRIX
IDENTIFIED**

HIGH PERFORMANCE POLYMER BLENDS

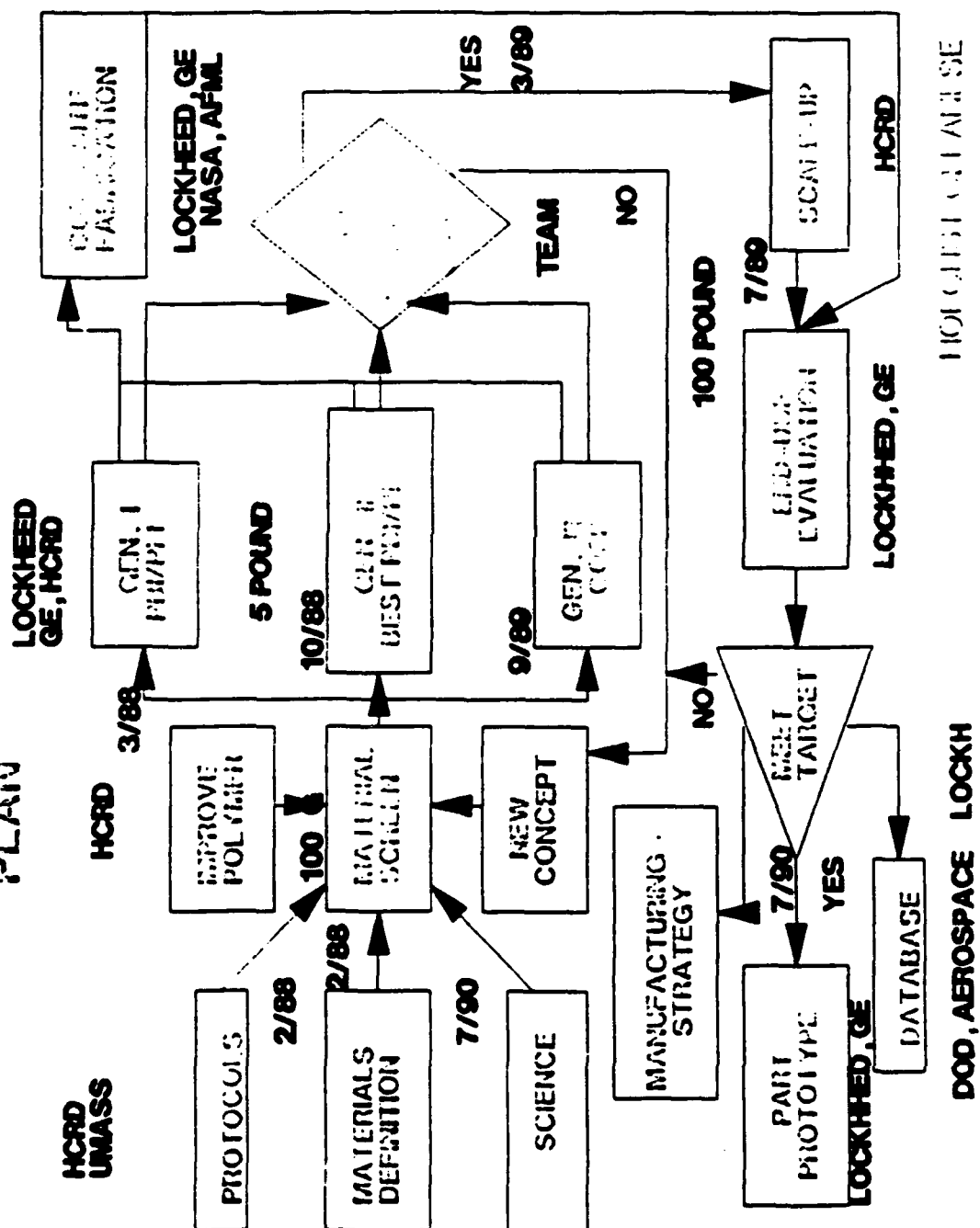
OBJECTIVES

- *DEVELOP PBI/PI BLENDS MEETING DOD/AEROSPACE REQUIREMENTS FOR A TOUGH, THERMO-PROCESSIBLE MATRIX FOR USE AT 400 - 700 F*
- DEVELOP A USER-RELEVANT MISCIBLE POLYMER BLEND DATABASE FOR AROMATIC HETEROCYCLIC AND MESOGENIC POLYMERS
- ADVANCE THE UNDERSTANDING OF MISCIBLE POLYMER BLENDS

DARPA/AFOSR

HOECHST CELANESE

CLAY



POLYMER BLENDS

PBI/PI MATERIALS APPROACH

ADVANTAGES

PBI

ULTEM

6F co PI

AVAILABLE

AVAILABLE

Tg > 300C

EASY TO PROCESS

EASY TO PROCESS

HIGH Tg: 430C

LOW MOISTURE
REGAIN

LOW MOISTURE REGAIN

HIGH COMP.
STR: 60 KSI

RETAINS PROPERTY
AT T

8-1-8

DISADVANTAGES

POOR TOS AT
T>500F

LOW Tg: 200C

POOR SOLVENT
RESISTANCE

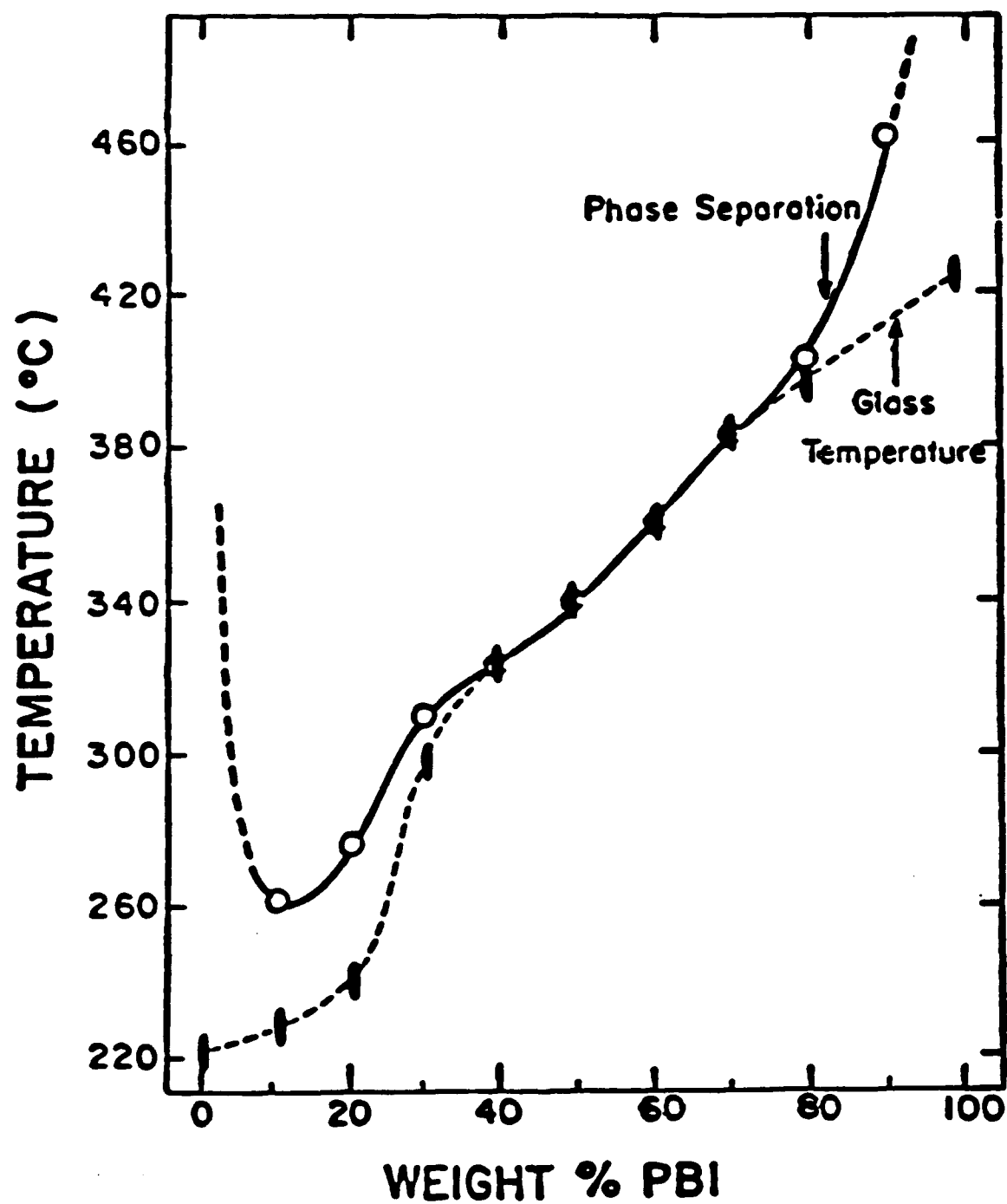
HIGH MOISTURE
REGAIN

HIGH COST

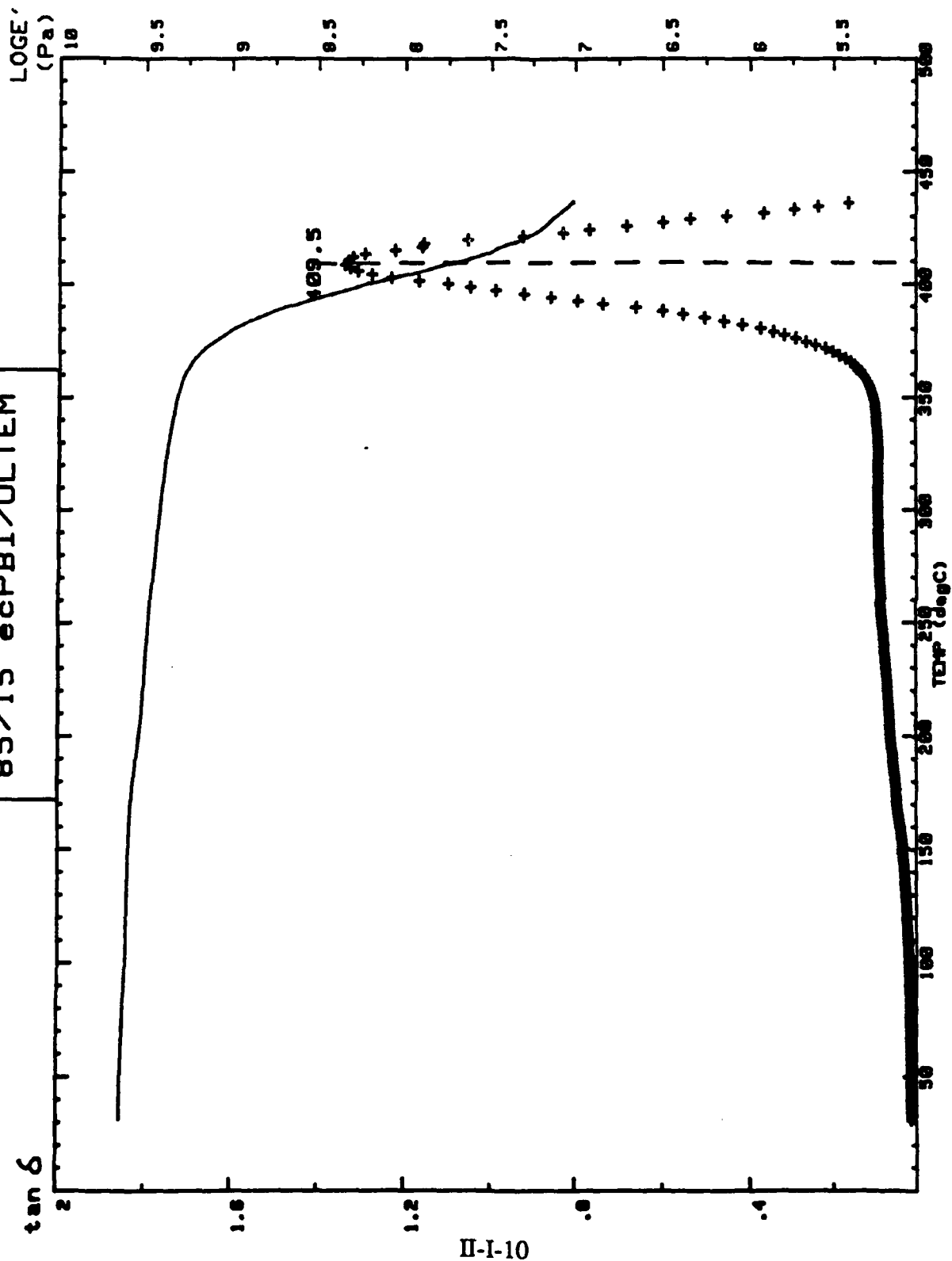
HARD TO PROCESS

HIGH COST

PBI/ULTEM PHASE DIAGRAM

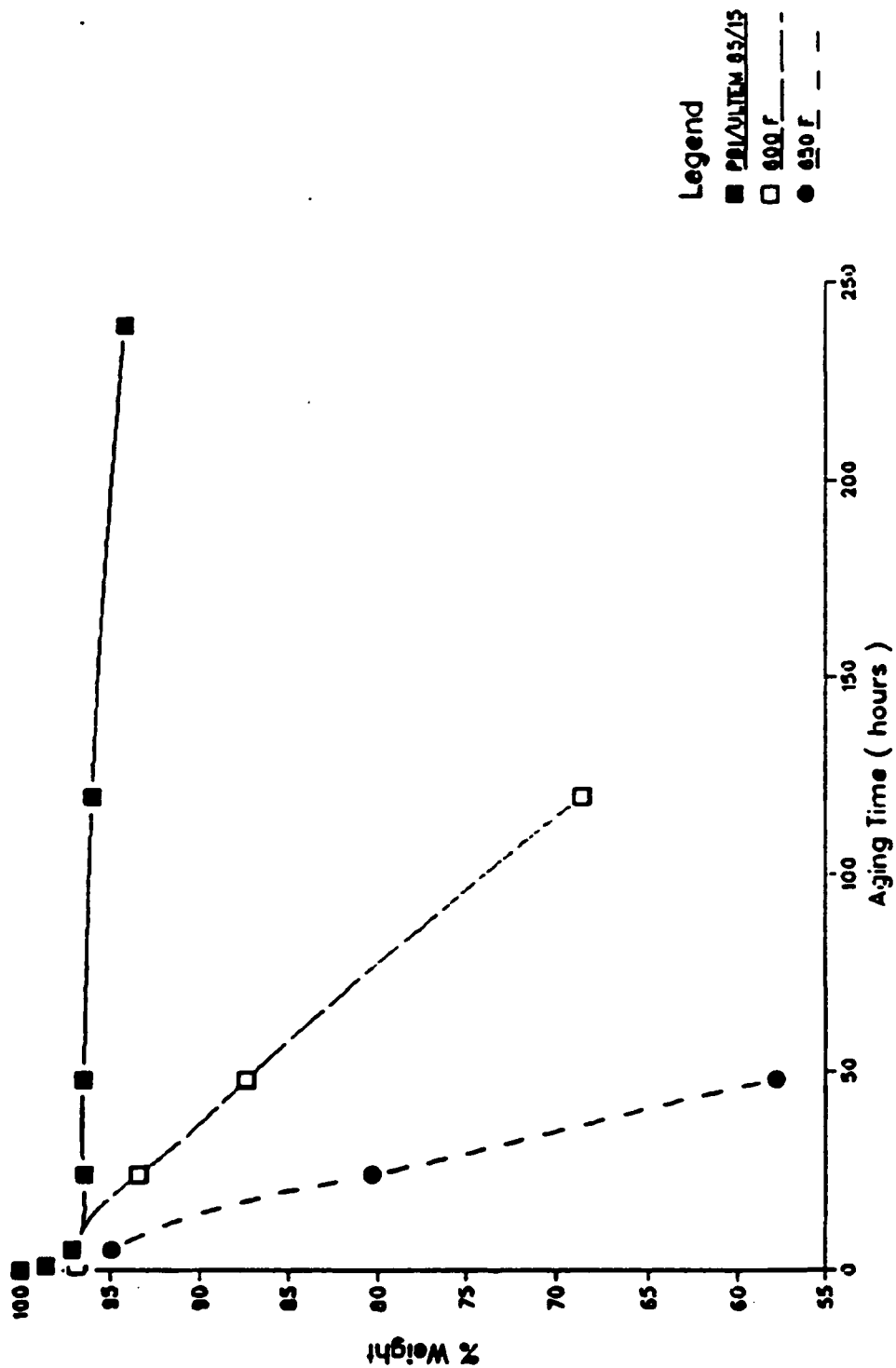


85/15 ecPBI/ULTEM



II-I-10

Thermo-Oxidative Stability of 85/15 PBI/ULTEM BLEND Fibers Aged in Air Oven at 500 F, 600 F AND 650 F



HIGH PERFORMANCE POLYMER BLENDS
MECHANICAL PROPERTIES OF ECPBI/ULTEM 85/15

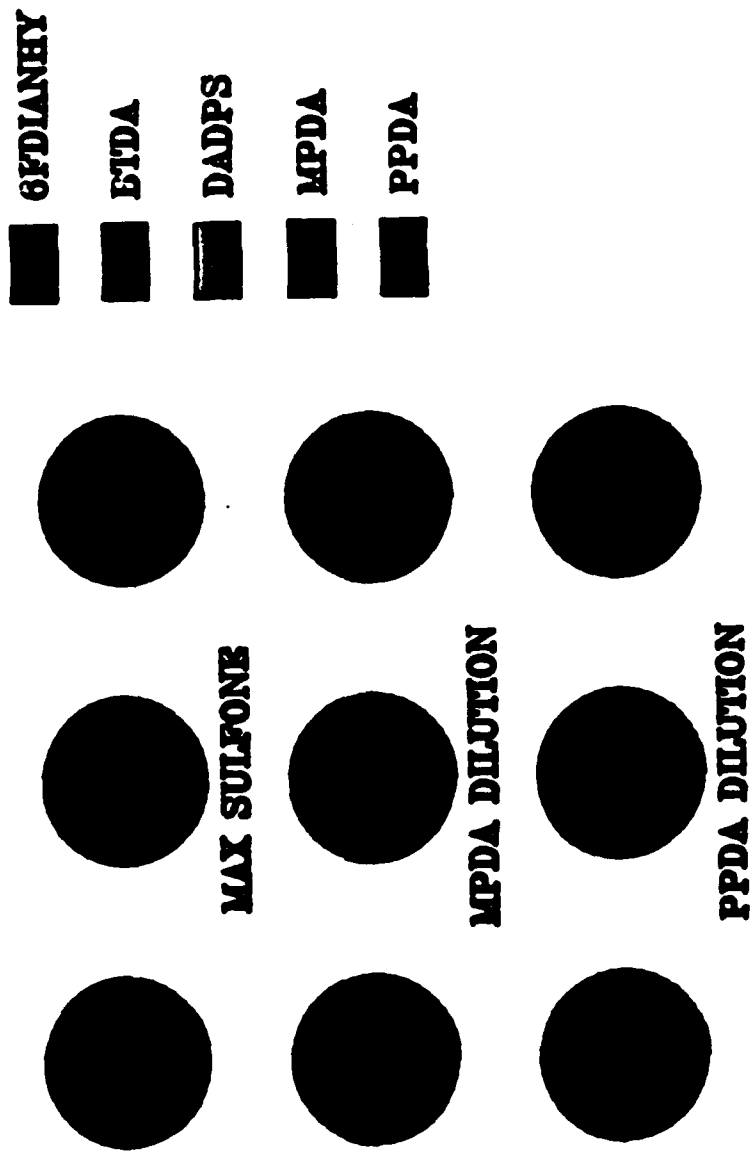
ROOM TEMPERATURE		
	STRENGTH (KSI)	ELONG (%) MOD (KSI)
TENSILE	23	3.4 780
FLEX		
COMPRESS.	43.5	750
AT TEMPERATURE (F)*		
75	23	780
250	17	700
350	15	680
450	14	600

*TENSILE TEST, 30 MINUTE SOAK AT TEMPERATURE IN AIR

HOECHST CELANESE

HIGH PERFORMANCE POLYMER BLENDS

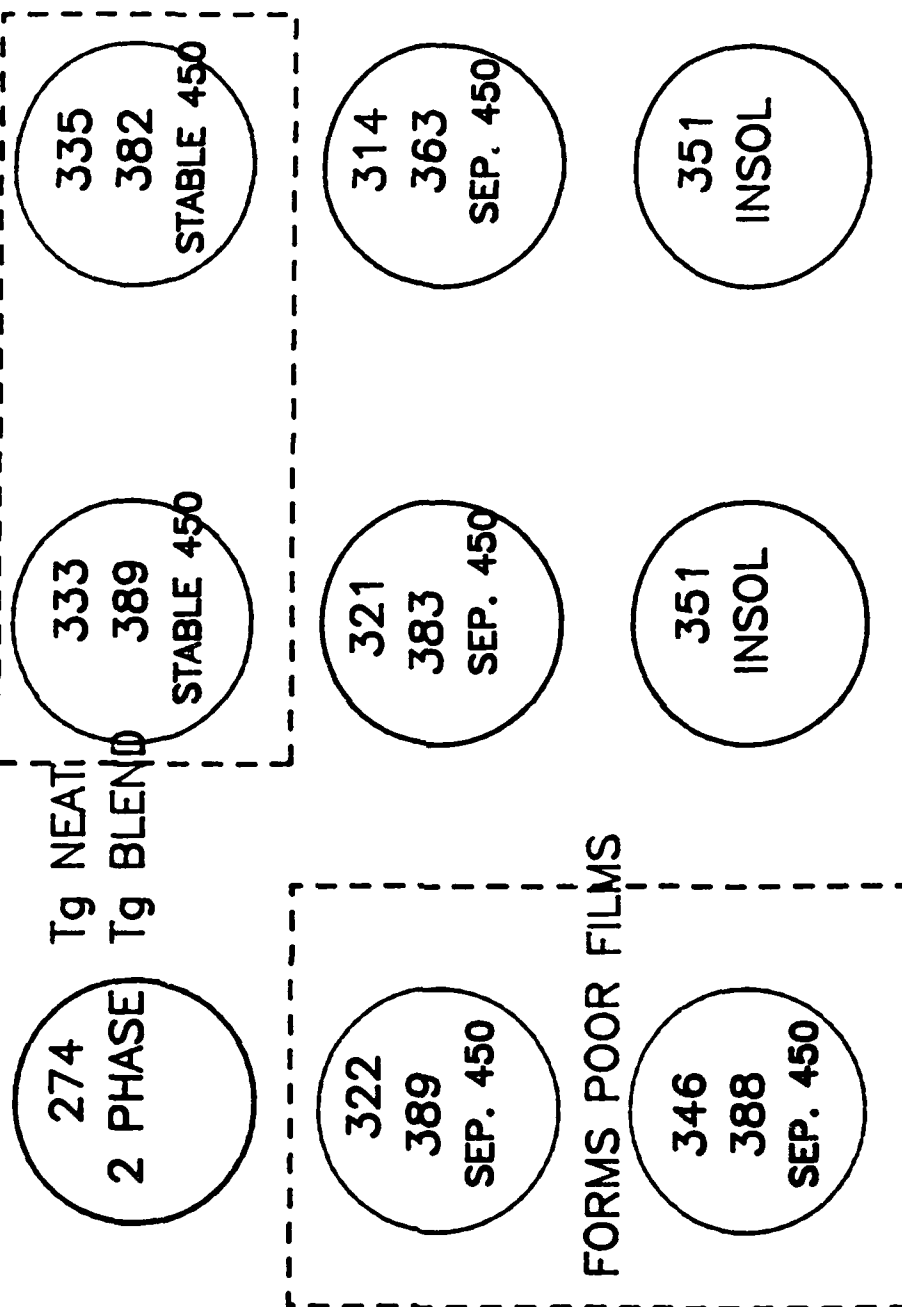
EXPERIMENTAL DESIGN - 6FCOPI
DIANH. - 6F,BTDA DIACID - m,p,PDA,DADPS



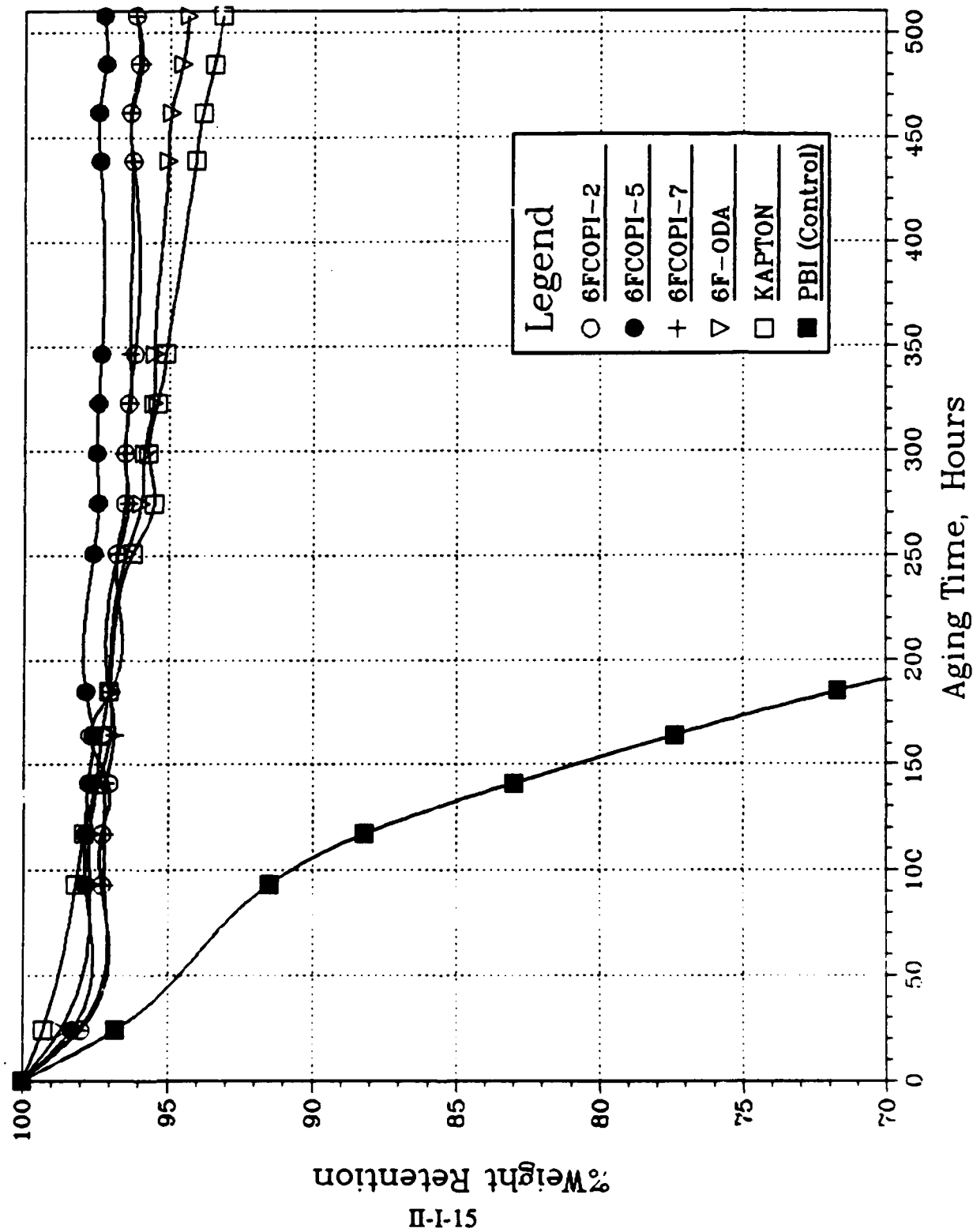
HOECHST CELANESE

50/50 PBI/6FPI BLENDS

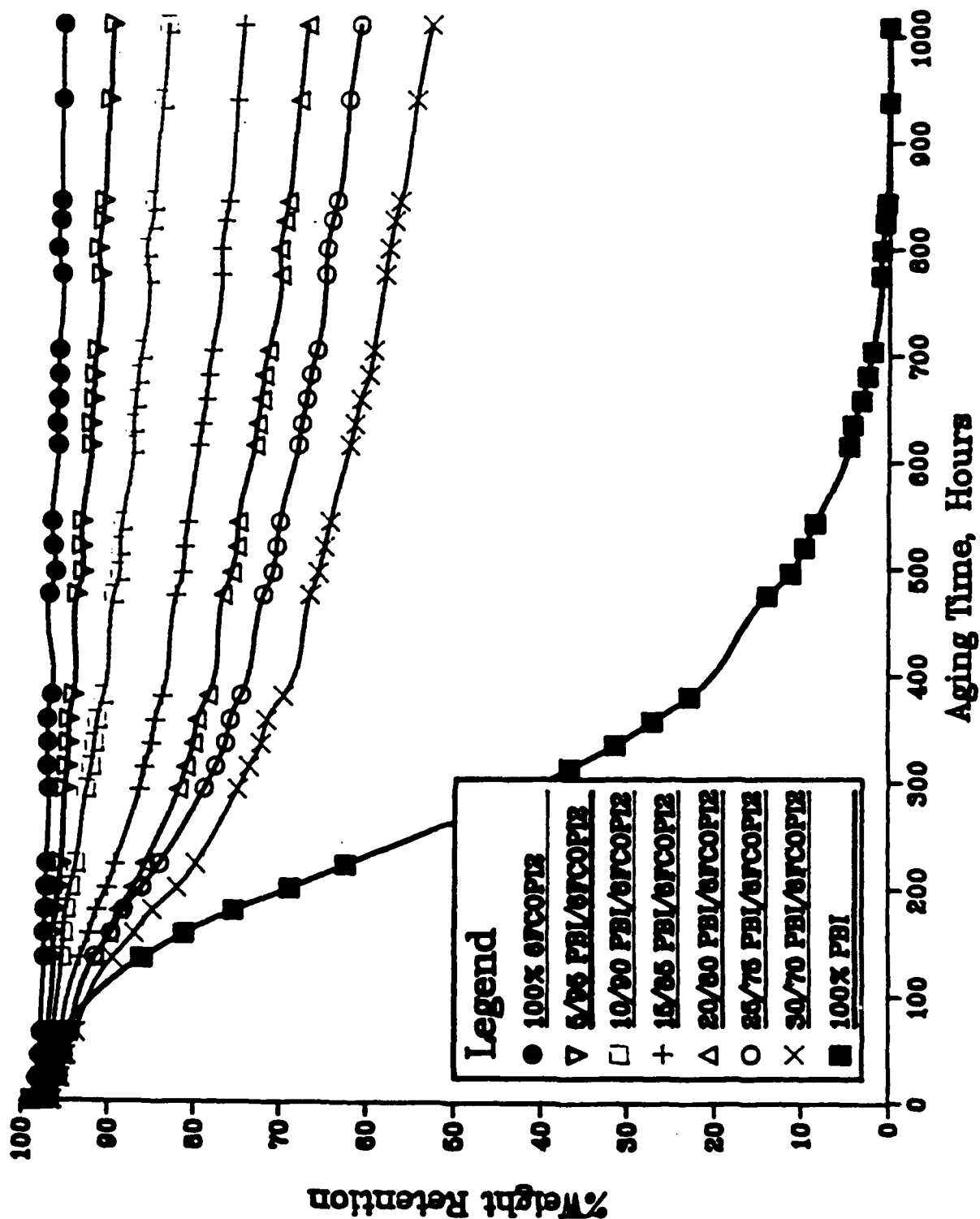
INITIAL CHARACTERIZATION



Thermo-Oxidative Stability of Neat 6F Copolymer Films Aged in Air Oven at 600 F



Thermo-Oxidative Stability of End Capped PBI and 6FCOP1-2 Blend Films Aged in Air Oven at 600 F



POLYMER BLENDS

10/90 ecPBI/6FcoPI2 MECHANICAL PROPERTIES

ROOM TEMPERATURE			
	STRENGTH (KSI)	MOD. (KSI)	ELONG (%)
TENSILE	14.4	507	4.1
FLEX	22.3	574	
COMP.	28	550	
500F			
(500 HOURS)			
TENSILE	12.8	500	3.2
600F			
(500 HOURS)			
TENSILE	10.7	500	2.4
			95.4
			98.6

POLYMER BLENDS

SCALE UP: 100 POUND SINGLE BATCH OF 6FcoPI2

PREPREG: SOLUTION PREPREGGING FROM DMAc ONTO AS-4
CARBON FABRIC AND UNIDIRECTIONAL TAPE

270 SQ. METERS - FABRIC (450 X 0.6)

41 SQ. METERS - TAPE (137 X 0.3)

II-I-18

**COMPOSITES: EVALUATIONS BY HOECHST CELANESE AND
LOCKHEED**

PART DEMONSTRATION BY LOCKHEED

POLYMER BLENDS CONCLUSIONS

- 85/15 END-CAPPED PBI/ULTEM(TM) BLEND IS A
VIABLE 500 F MATRIX CANDIDATE**

POLYMER BLENDS CONCLUSIONS

- **85/15 END-CAPPED PBI/ULTEM(TM) BLEND IS A
VIABLE 500 F MATRIX CANDIDATE**
- **10/90 END-CAPPED PBI/6FCOPI2 BLEND IS A
VIABLE 600 F MATRIX CANDIDATE**

POLYMER BLENDS CONCLUSIONS

- 85/15 END-CAPPED PBI/ULTEM(TM) BLEND IS A VIABLE 500 F MATRIX CANDIDATE
- 10/90 END-CAPPED PBI/6FCOPI2 BLEND IS A VIABLE 600 F MATRIX CANDIDATE
- ALL PBI/PI SYSTEMS EXHIBIT MISCIBILITY WHICH:
 - EXHIBIT IMPROVED PROCESSIBILITY OVER NEAT PBI
 - ARE THERMOFORMABLE
 - HAVE IMPROVED MECHANICAL PERFORMANCE, ESPECIALLY IN COMPRESSION
 - HAVE IMPROVED SOLVENT RESISTANCE AS COMPARED TO THERMOPLASTIC POLYIMIDES

POLYMER BLENDS CONCLUSIONS

- ***MISCIBILITY IS METASTABLE, HOWEVER PHASE SEPARATION DOES NOT APPEAR TO BE DETRIMENTAL***

POLYMER BLENDS CONCLUSIONS

- **MISCIBILITY IS METASTABLE, HOWEVER PHASE SEPARATION DOES NOT APPEAR TO BE DETRIMENTAL**
- **PBI/PI BLENDS EXHIBIT NEGATIVE THERMO-OXIDATIVE SYNERGY WHICH IS MITIGATED BY CHOICE OF HIGH TOS POLYIMIDE**
 - **6FCOPI2 SHOWS ~5% WEIGHT LOSS AFTER 1000 HOURS AT 600 F**
 - **DEGRADATION REACTIONS ARE EXACERBATED BY MISCIBILITY**
(SIMILAR TO HOMOGENEOUS REACTION)
 - **PHOSPHORIC ACID SURFACE TREATMENT IMPROVES TOS FOURFOLD**

POLYMER BLENDS CONCLUSIONS

- ***PBI/PI BLENDS CAN BE SOLUTION PREPREGGED
ONTO CARBON FABRIC AND TOW AND THEN
THERMALLY FORMED INTO PARTS***

POLYMER BLENDS CONCLUSIONS

- **PBI/PI BLENDS CAN BE SOLUTION PREPREGGED ONTO CARBON FABRIC AND TOW AND THEN THERMALLY FORMED INTO PARTS**
- ***6FCOPI2 CAN BE SYNTHESIZED IN LARGE QUANTITIES SUITABLE FOR MEANINGFUL AEROSPACE PART FABRICATION AND EVALUATION***

POLYMER BLENDS

RECOMMENDATIONS

- **RESEARCH:**
 - BLENDING IS A VIABLE APPROACH TO MATRIX TAILORING
 - THE ISSUE OF BACKBONE OPTIMIZATION FOR NEW POLYMERS SHOULD BE PURSUED, BALANCING PERFORMANCE AND COST
 - BLEND CRITERIA DEVELOPED IN THIS PROGRAM SHOULD BE EXTENDED TO SYSTEMS NOT INCORPORATING PBI (I.E. PBO, ETC.)
- **DEVELOPMENT:**
 - THE OPTIMIZATION OF THE POLYIMIDE BACKBONE FOR TOS AND PROCESSIBILITY SHOULD BE PURSUED, EMPHASIZING GF
 - ADDRESS QUESTION OF PREDICTION OF REAL SYSTEM PERFORMANCE FROM LABORATORY SAMPLES
- **FABRICATION:**
 - FUTURE PROGRAMS SHOULD RECOGNIZE THAT IT IS COMPOSITE COST/PERFORMANCE RATHER THAN MATERIAL PROPERTIES THAT DEFINE MATRIX UTILITY
- **ORGANIZATION:**
 - THE INTERDISCIPLINARY, INTERSECTOR TEAM APPROACH TO THE RAPID TRANSLATION OF SCIENCE TO TECHNOLOGY IS EFFECTIVE AND EFFICIENT AND SHOULD BECOME THE PARADIGM FOR THE ORGANIZATION OF LARGE, HIGHLY FOCUSED MATERIALS DEVELOPMENT PROGRAMS

UNIVERSITY OF SOUTHERN CALIFORNIA

Professor Eric J. Amis

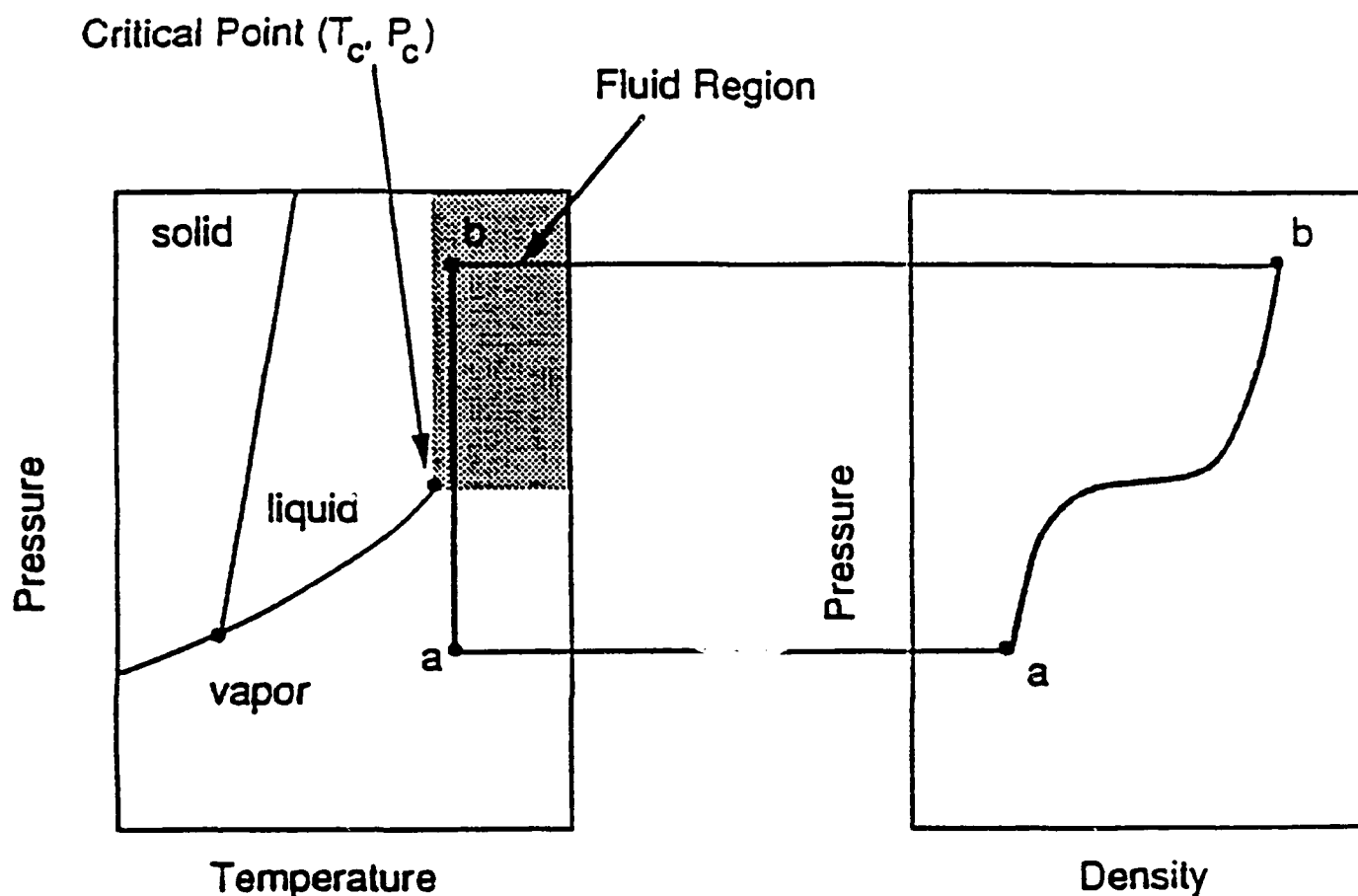
Processing of Polymers Using Supercritical Fluids

John J. Aklonis and Eric J. Amis

*Department of Chemistry
University of Southern California
Los Angeles, California*

- Introduction to supercritical fluids
- Solubility properties
- Polymer solubilities
- Forming materials from supercritical solutions
- Characterizations of polymers in supercritical solutions

Solvent density in SCF region



Pressure dependence on SCF density

Because solvating power of a fluid depends on its density, the solvating power of an SCF can be varied over a wide range by variations in pressure

Applications of supercritical fluids

Coffee decaffeination

Spice extraction

Extraction of residual solvents, reactants, catalysts

Fractionation of low vapor-pressure materials

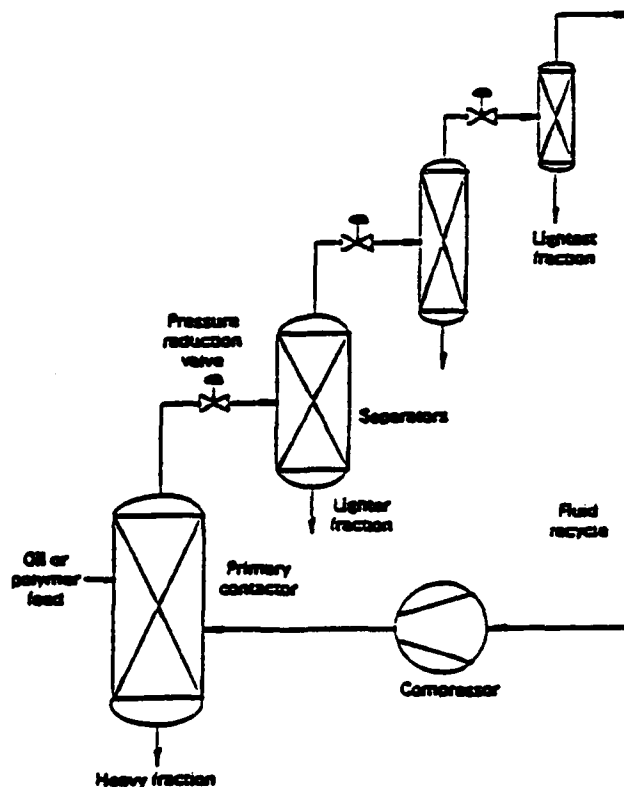


Fig. 8. Continuous supercritical fluid fractionation process.

Chromatographic separations of oligomers

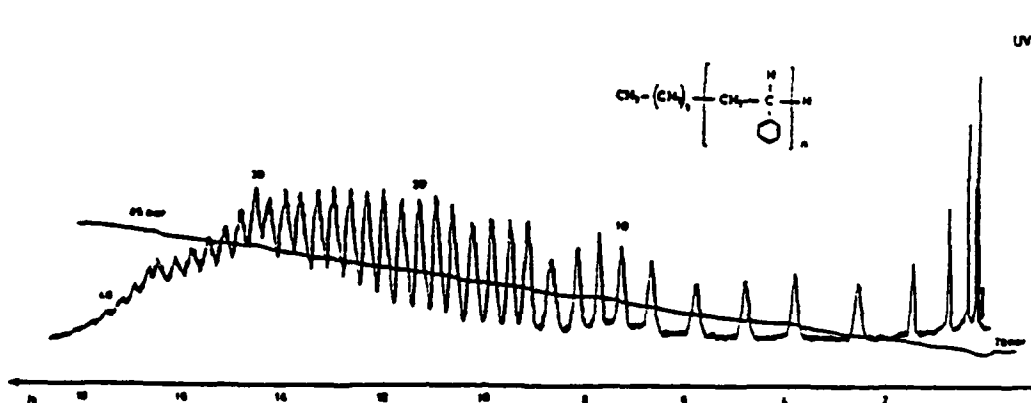
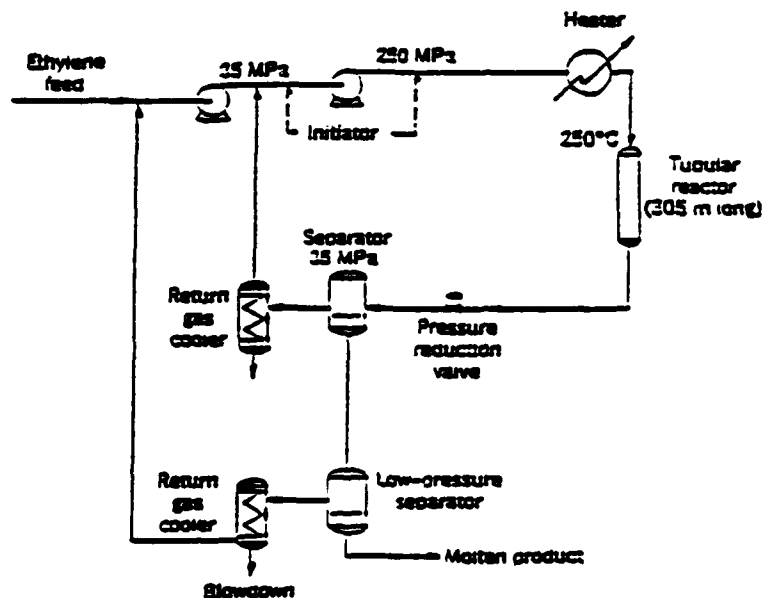


Fig. 3. Chromatographic run of oligostyrene of nominal $M_n = 3200$ (PCC) in a 3 mm I.D. column. A solution 100- μ l containing 40 mg oligostyrene in cyclohexane was injected. Feed rate, 3.1 ml/min; pressure program starting at 28 bar and increasing at a rate of 3.3 bar/hr; column dimensions, 6 m \times 3 mm I.D.

Polymerization of low density polyethylene

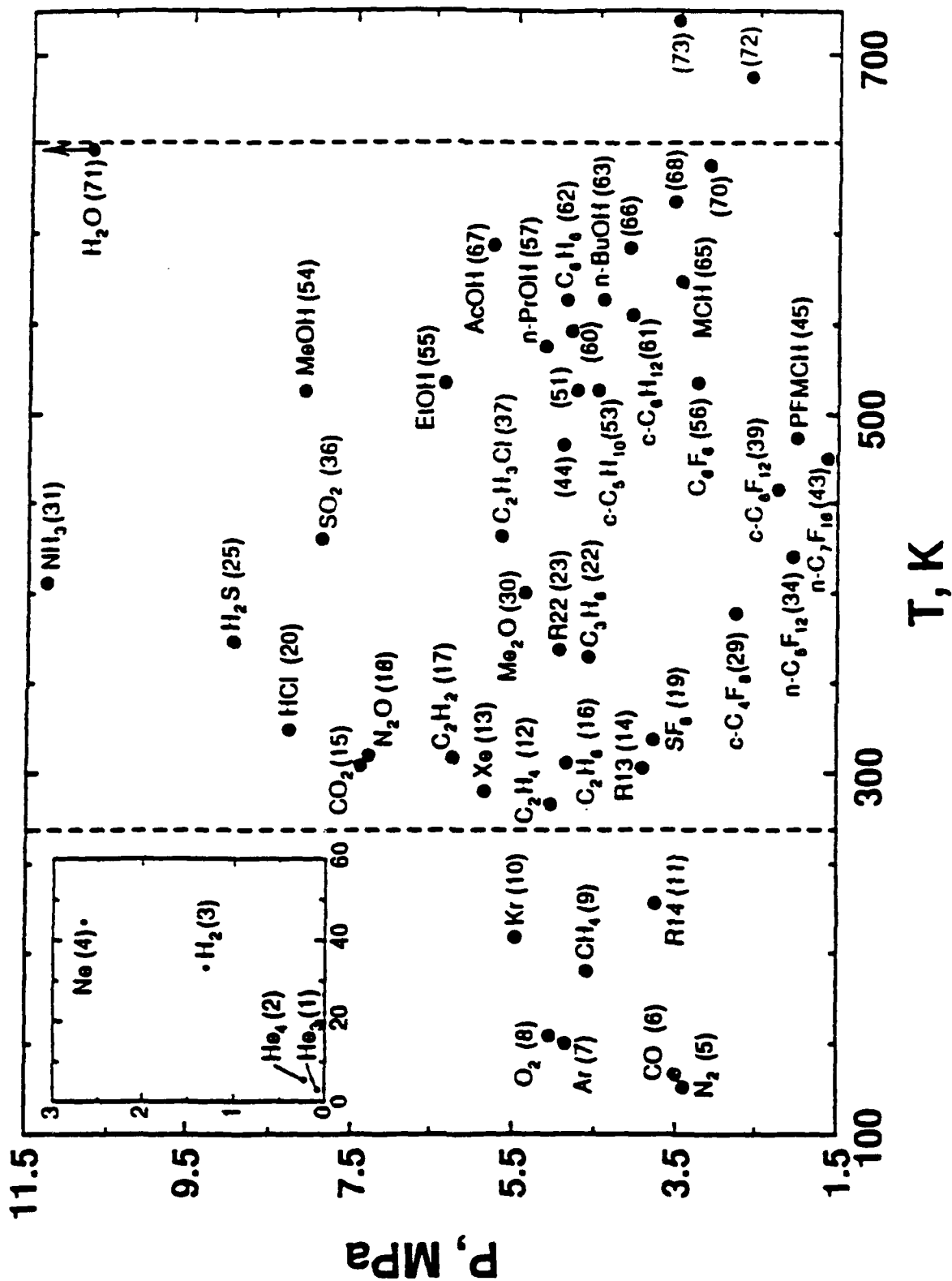


Destruction of toxic waste with supercritical water

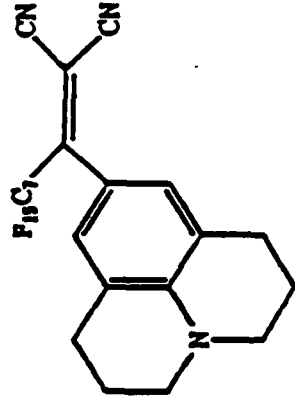
TABLE A "Primary" Pure Fluids

Fluid	Abbrev.	T _b /K	P _b /MPa	No. of mixtures
1. Helium 3	He ₃	3.311	0.115	1
2. Helium 4	He ₄	5.188	0.227	1
3. Hydrogen	H ₂	33.25	1.297	1
4. Neon*	Ne	44.40	2.654	1
5. Nitrogen*	N ₂	126.24	3.398	1
6. Carbon monoxide*	CO	132.85	3.494	1
7. Argon*	Ar	150.66	4.860	1
8. Oxygen*	O ₂	154.58	5.043	1
9. Methane*	CH ₄	190.55	4.595	11
10. Krypton	Kr	209.46	5.49	5
11. Carbon tetrafluoride	R14	227.6	3.74	1
12. Ethylene*	C ₂ H ₄	282.35	5.040	10
13. Xenon	Xe	289.7	5.87	3
14. Chlorotrifluoromethane	R13	302.0	3.92	1
15. Carbon dioxide*	CO ₂	304.17	7.386	26
16. Ethane*	C ₂ H ₆	305.34	4.871	17
17. Acetylene	C ₂ H ₂	308.70	6.247	3
18. Nitrous oxide	N ₂ O	309.15	7.285	3
19. Sulfur hexafluoride	SF ₆	318.82	3.765	1
20. Hydrogen chloride	HCl	324.55	8.263	3
21. Bromotrifluoromethane	R13B1	340.08	3.956	1
22. Propylene	C ₃ H ₆	365.05	4.600	5
23. Chlorodifluoromethane	R22	369.27	4.967	4
24. Propane*	C ₃ H ₈	369.85	4.247	21
25. Hydrogen sulfide	H ₂ S	373.40	8.963	5
26. Trifluoropropylene	C ₃ H ₃ F ₃	376.2	3.80	1
27. Dichlorodifluoromethane	R12	385.01	4.129	1
28. 1,1-Difluoroethane	R152a	386.44	4.520	1
29. Perfluorocyclobutane	c-C ₄ F ₈	388.43	2.785	1
30. Dimethyl ether	Me ₂ O	400.10	5.370	5
31. Ammonia	NH ₃	405.45	11.278	5
32. Isobutane*	i-C ₄ H ₁₀	407.84	3.629	5
33. Dichlorotetrafluoroethane	R114	418.86	3.220	3
34. Perfluoro-n-pentane	n-C ₅ F ₁₂	420.59	2.045	1
35. n-Butane*	n-C ₄ H ₁₀	425.38	3.809	15
36. Sulfur dioxide	SO ₂	430.75	7.884	2
37. Vinyl chloride	C ₂ H ₃ Cl	432.00	5.670	1
38. Neopentane	nen-C ₅ H ₁₂	433.75	3.196	2
39. Perfluorocyclohexane	c-C ₆ F ₁₂	457.29	2.237	1
40. Isopentane*	i-C ₅ H ₁₂	460.51	3.371	2
41. Diethyl ether	Et ₂ O	466.56	3.651	1
42. n-Pentane*	n-C ₅ H ₁₂	469.65	3.370	8
43. Perfluoro-n-heptane	n-C ₇ F ₁₆	474.85	1.636	4
44. Epoxyp propane (propylene oxide)	—	482.25	4.924	1
45. Perfluoromethylcyclohexane	PFMCH	485.90	2.019	5
46. 2,2-Dimethyl butane	22DMB	489.25	3.102	2
47. 2-Methyl pentane*	2MP	498.05	3.035	2
48. 2,3-Dimethyl butane	23DMB	500.23	3.147	2
49. 3-Methyl pentane	3MP	504.62	3.128	2
50. n-Hexane*	n-C ₆ H ₁₄	507.95	3.032	4
51. Acetone	Me ₂ CO	508.15	4.758	2
52. Isopropanol	i-PrOH	508.31	4.764	1
53. Cyclopentane	c-C ₅ H ₁₀	511.76	4.502	1
54. Methanol	MeOH	512.58	8.097	4
55. Ethanol	EtOH	516.25	6.384	2
56. Perfluorobenzene	C ₆ F ₆	516.71	3.275	2
57. n-Propanol	n-PrOH	536.70	5.142	1
58. n-Heptane*	n-C ₇ H ₁₆	540.00	2.736	6
59. Iso-octane (2,2,4-trimethylpentane)	i-C ₈ H ₁₈	543.83	2.564	1
60. Acetonitrile	CH ₃ CN	545.50	4.833	1
61. Cyclohexane	c-C ₆ H ₁₂	553.54	4.075	2
62. Benzene	C ₆ H ₆	562.24	4.888	9
63. n-Butanol	n-BuOH	562.89	4.416	3
64. n-Octane	n-C ₈ H ₁₈	569.20	2.603	3
65. Methylcyclohexane	MCH	572.2	3.47	1
66. Toluene	—	591.79	4.109	2
67. Acetic acid	AcOH	592.71	5.786	1
68. m-Xylene	—	617.05	3.541	1
69. n-Decane	n-C ₁₀ H ₂₂	619.3	2.096	4
70. Mesitylene	—	637.3	3.13	1
71. Water	H ₂ O	647.29	22.09	3
72. trans-Decalin	—	687.1	2.615	1
73. Tetralin	—	719.2	3.515	1

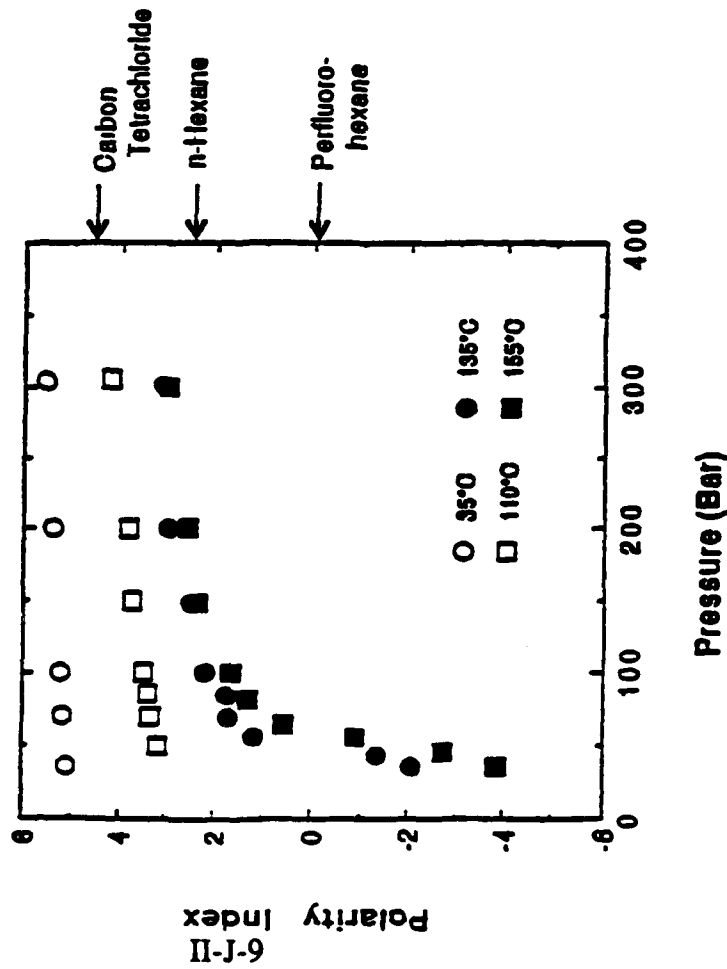
* Included in the package DOMIX as of 2/91.



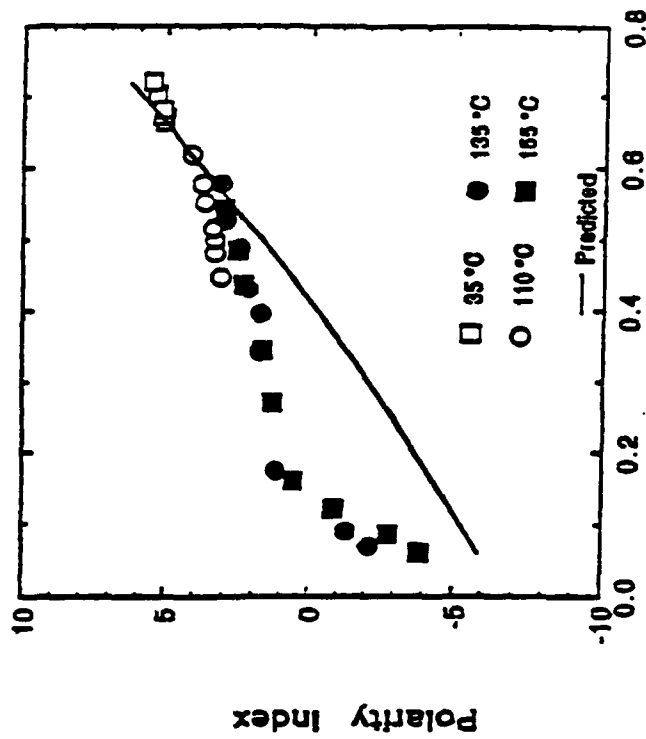
Variation of SCF solvent polarity with pressure



9-(α -perfluoroheptyl- β,β -dicyanovinyl)julolidine



Polarity index of sub and supercritical dimethyl ether determined by spectral shift of dye

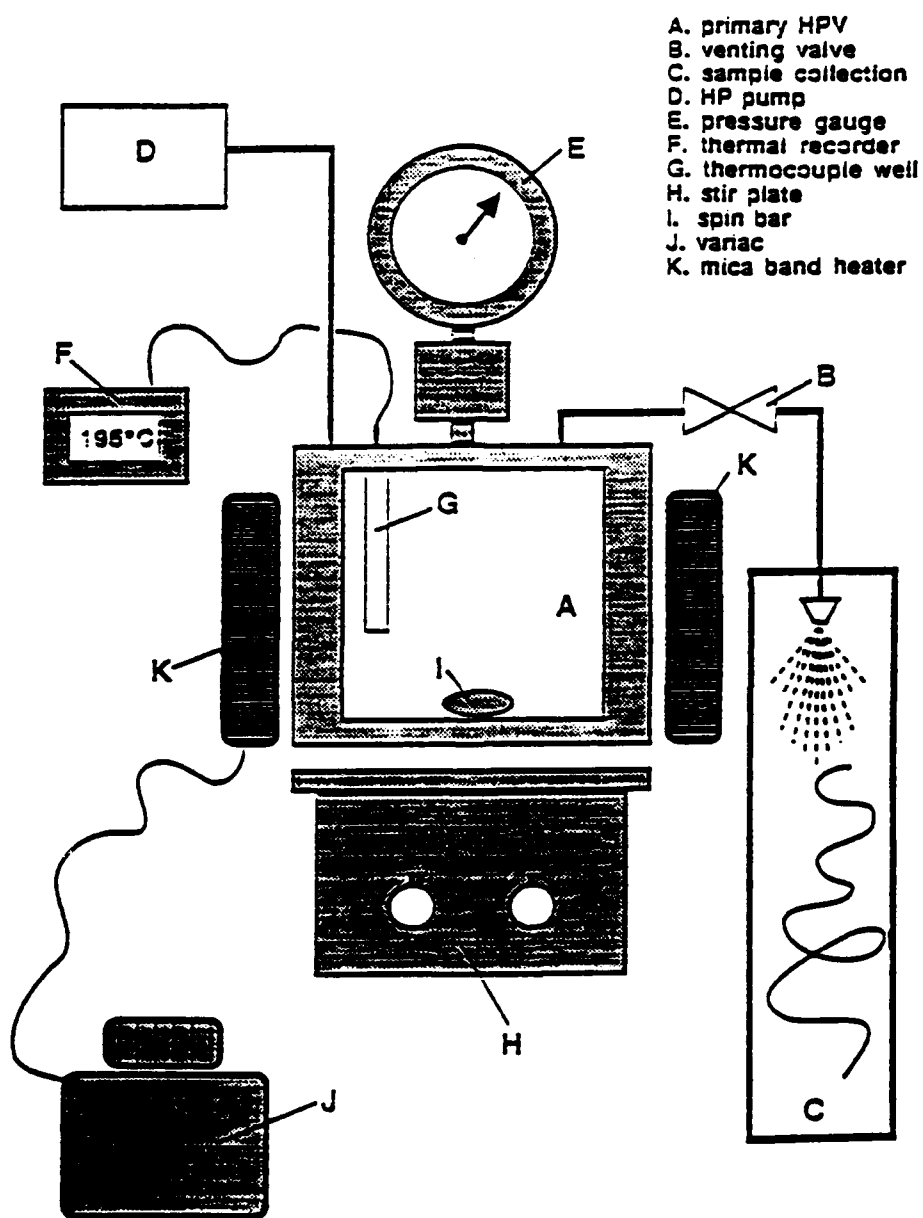


Density (g/cc)

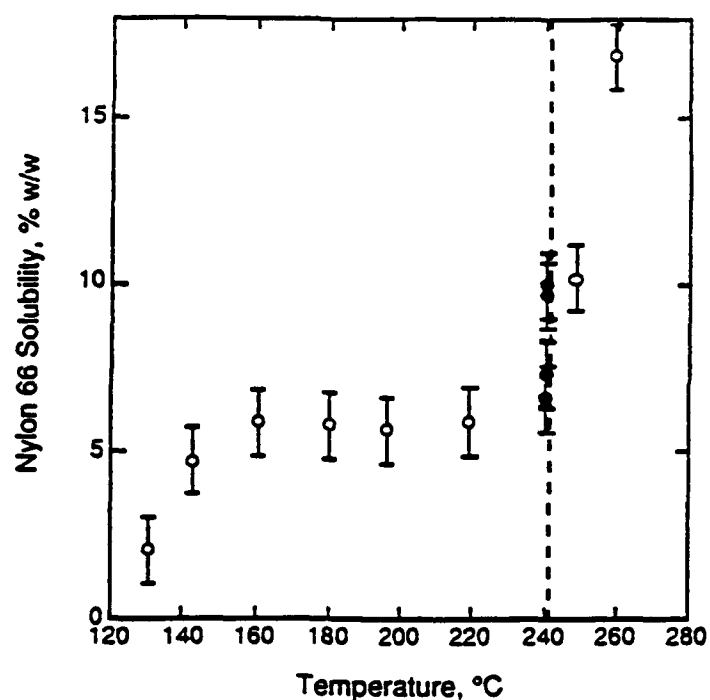
Measured and predicted values of solvent polarity as a function of density for dimethyl ether

(from R. M. Lemert and J. M. DeSimone, J. Supercritical Fluids, 1992)

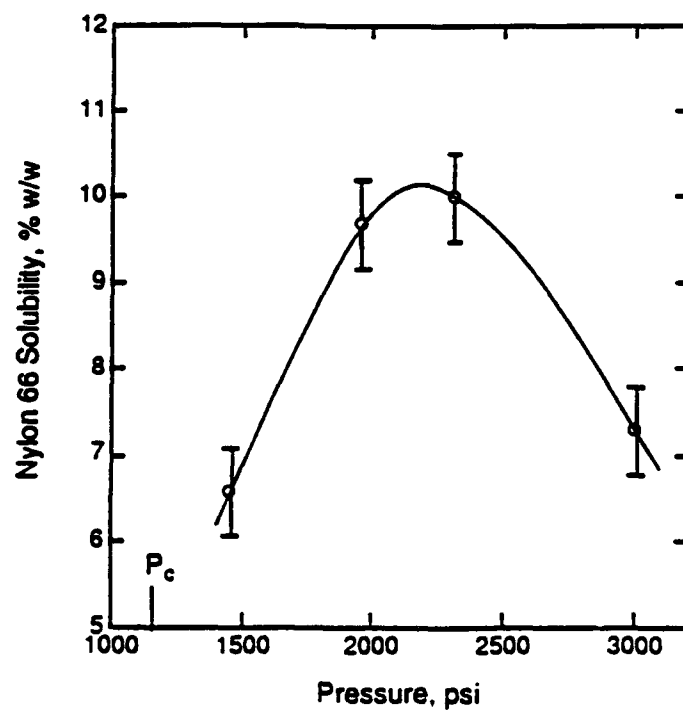
Schematic of SCF setup



Nylon 6,6 in methanol



Solubility increases with temperature past the critical point



Maximum in solubility with pressure past the critical point

Polyethylene and polypropylene

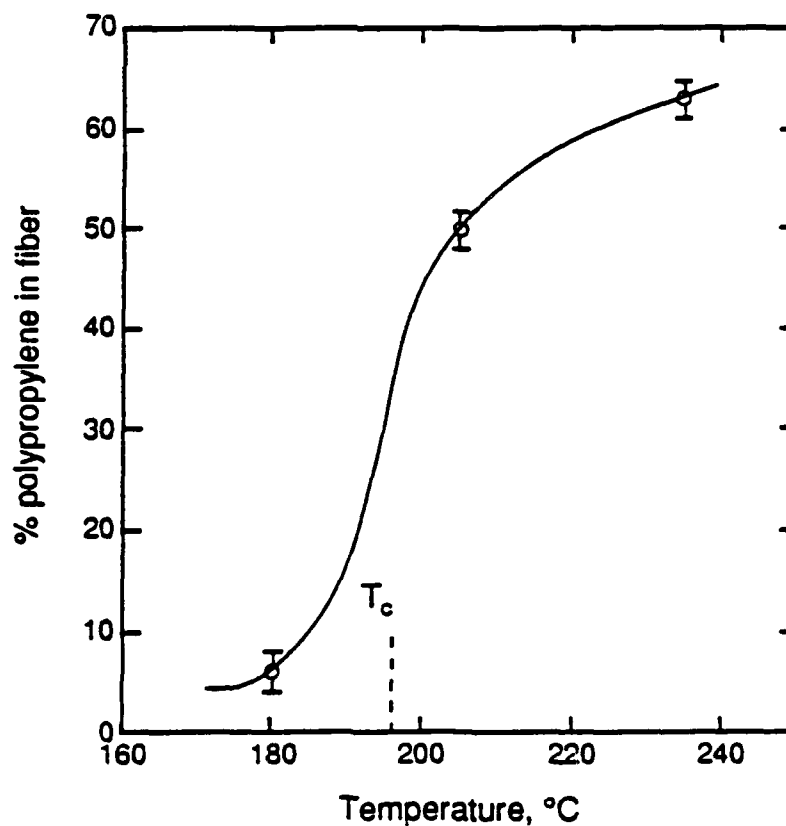
Samples:

PP fiber from pentane supercritical fluid,
198°C and 3000 psi

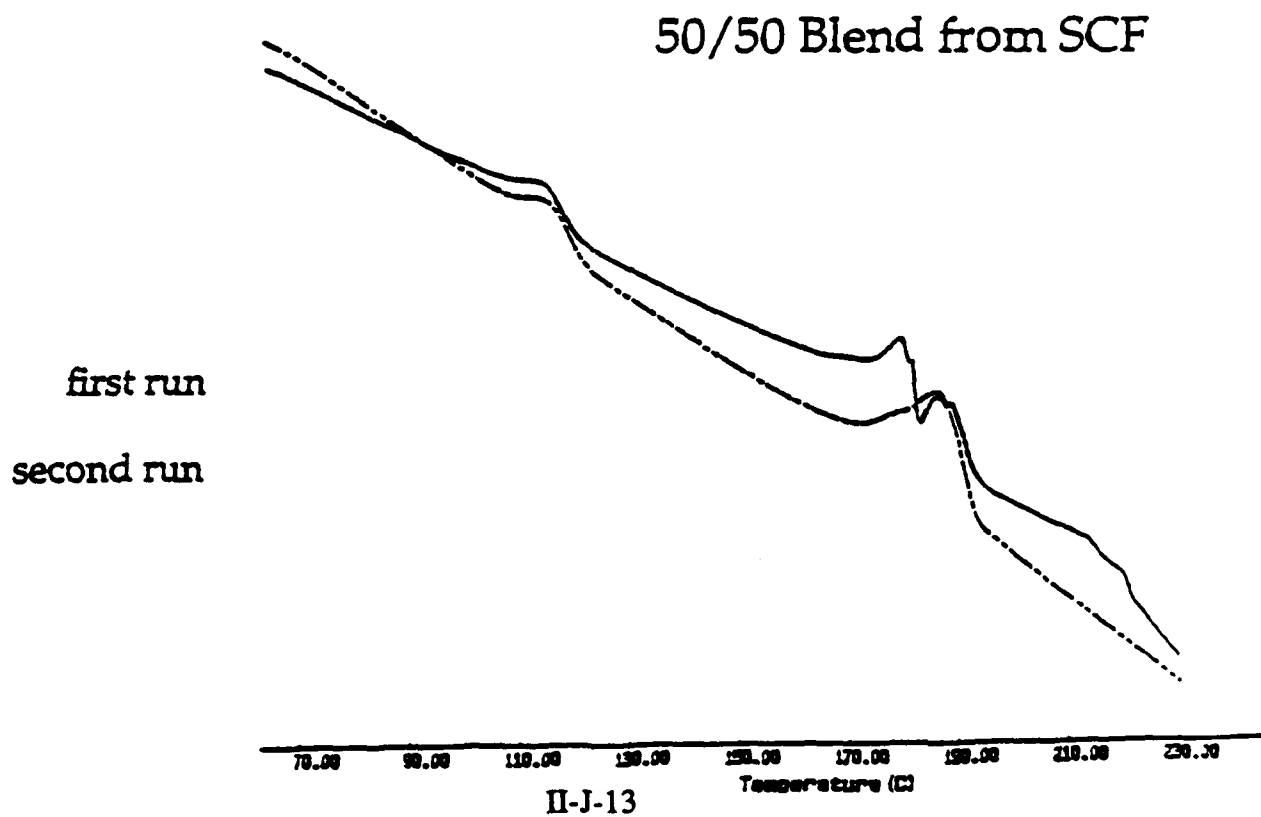
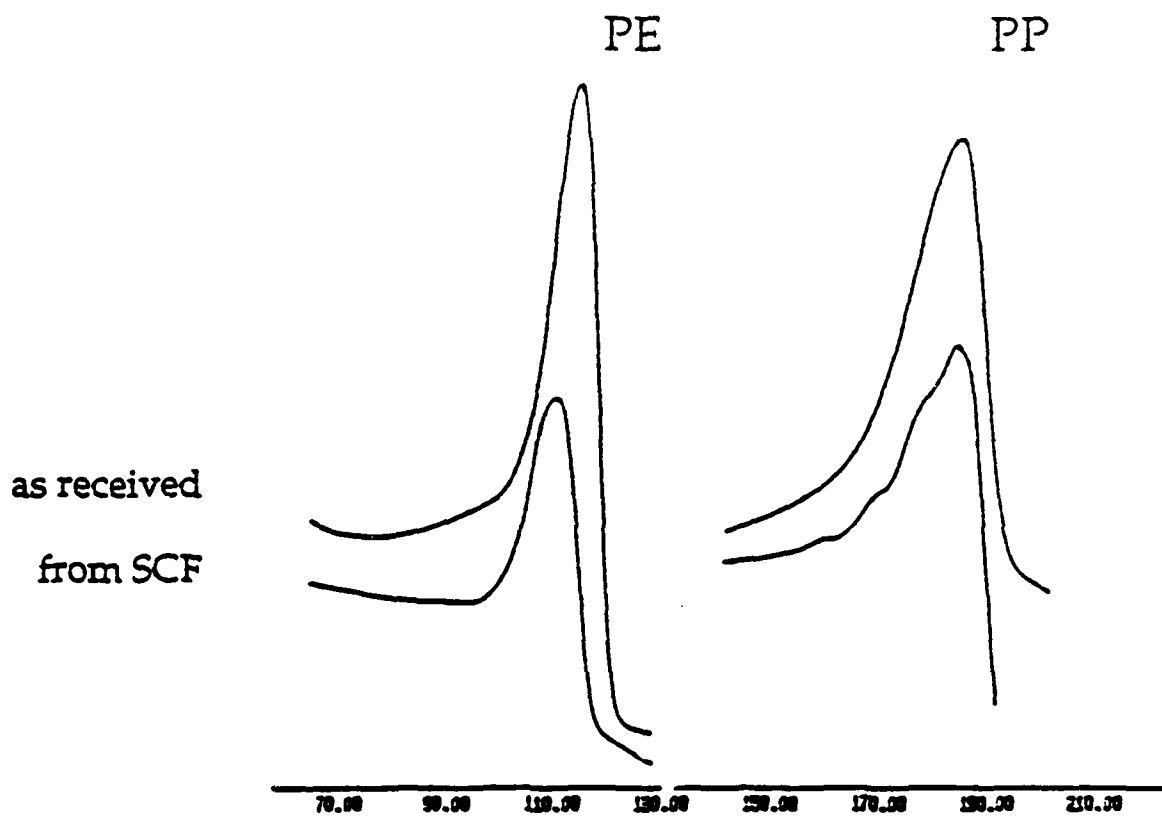
50/50 blend from pentane subcritical,
120°C and 3000 psi

50/50 blend from pentane supercritical fluid,
198°C and 3000 psi

Composition of fiber from SCF solutions



DSC on PE, PP, and Blend



II-J-13

Examples

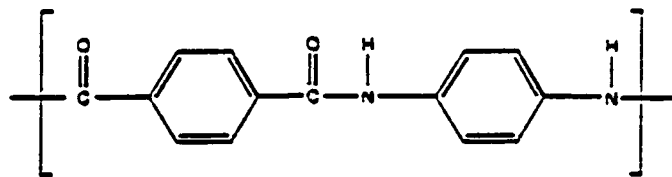
polymer	solvent	comments
PE	pentane ethane, propane, butane	very soluble, fiber formation soluble, requires higher P
PP	pentane ethane, propane, butane	very soluble, fiber formation soluble, requires higher P
nylon 6/6	methanol	increasing solubility with T, powder formation
nylon 6	methanol	increasing solubility with T, powder formation
PS	pentane	extraction of low MW material
PαMS	pentane	extraction of low MW material
PVA	methanol	highly soluble, reacts to form PVOH at high T
PET	methanol pentane	highly soluble, degrades to low MW at high T. insoluble at all T and P
PMMA	methanol pentane	solubility >10% at T _C insoluble at all T and P
ULTEM	methanol	swells slightly and extracts low MW material near T _C
Vectra	methanol/pentane	swells slightly and extracts low MW material near T _C
Kevlar	methanol	insoluble at all T and P
substituted polyaramide	methanol	soluble near T _C

Difficult materials

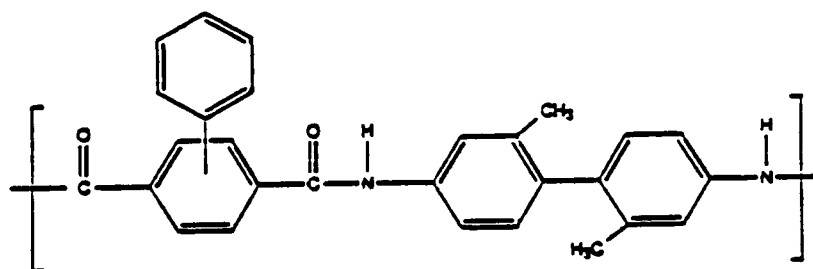
Ultra-high molecular weight polyethylene

- 3×10^6 MW dissolves in supercritical pentane at concentrations high enough for gel formation

PPTA type materials



- Commercial Kevlar (DuPont) soluble in H_2SO_4
swells slightly in supercritical methanol
no weight loss, no change in η_{inh}



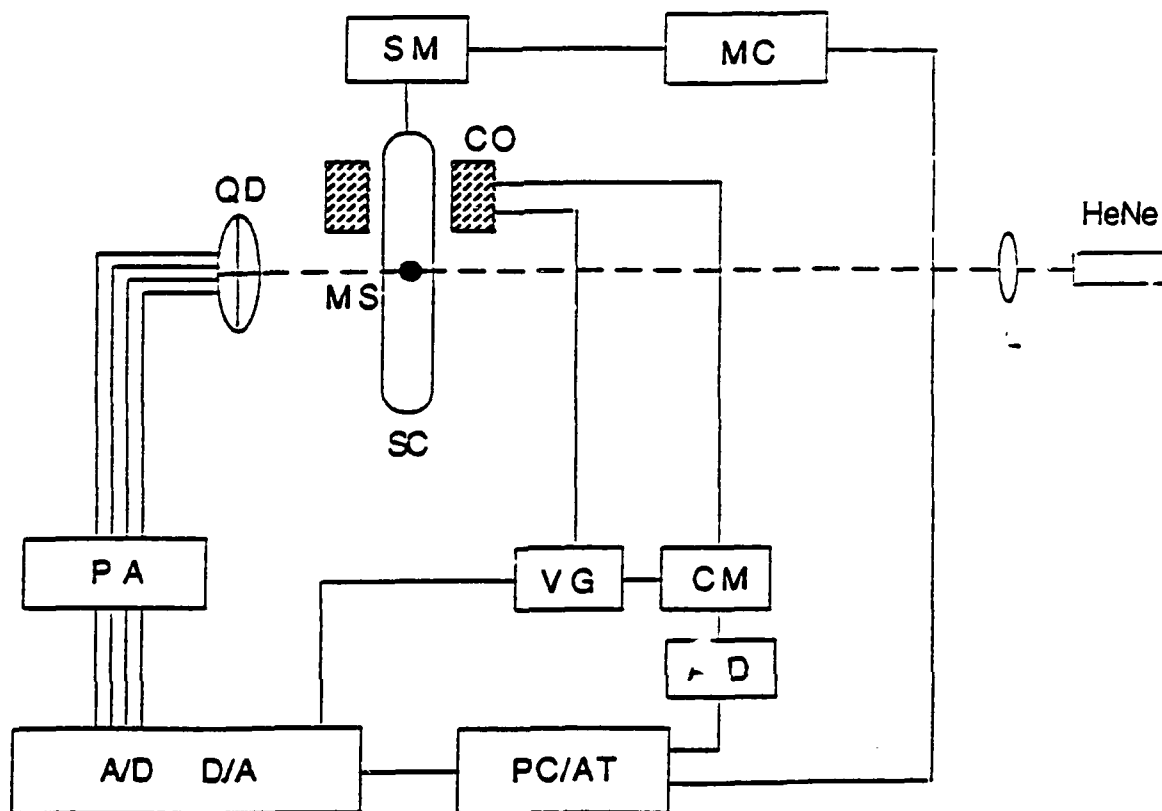
- Substituted polyaramide soluble in H_2SO_4 ,
DMAc/LiCl, and DMAc,
soluble in supercritical methanol
no weight loss

in collaboration with H.-W. Schmidt (UC Santa Barbara)

PBO type materials

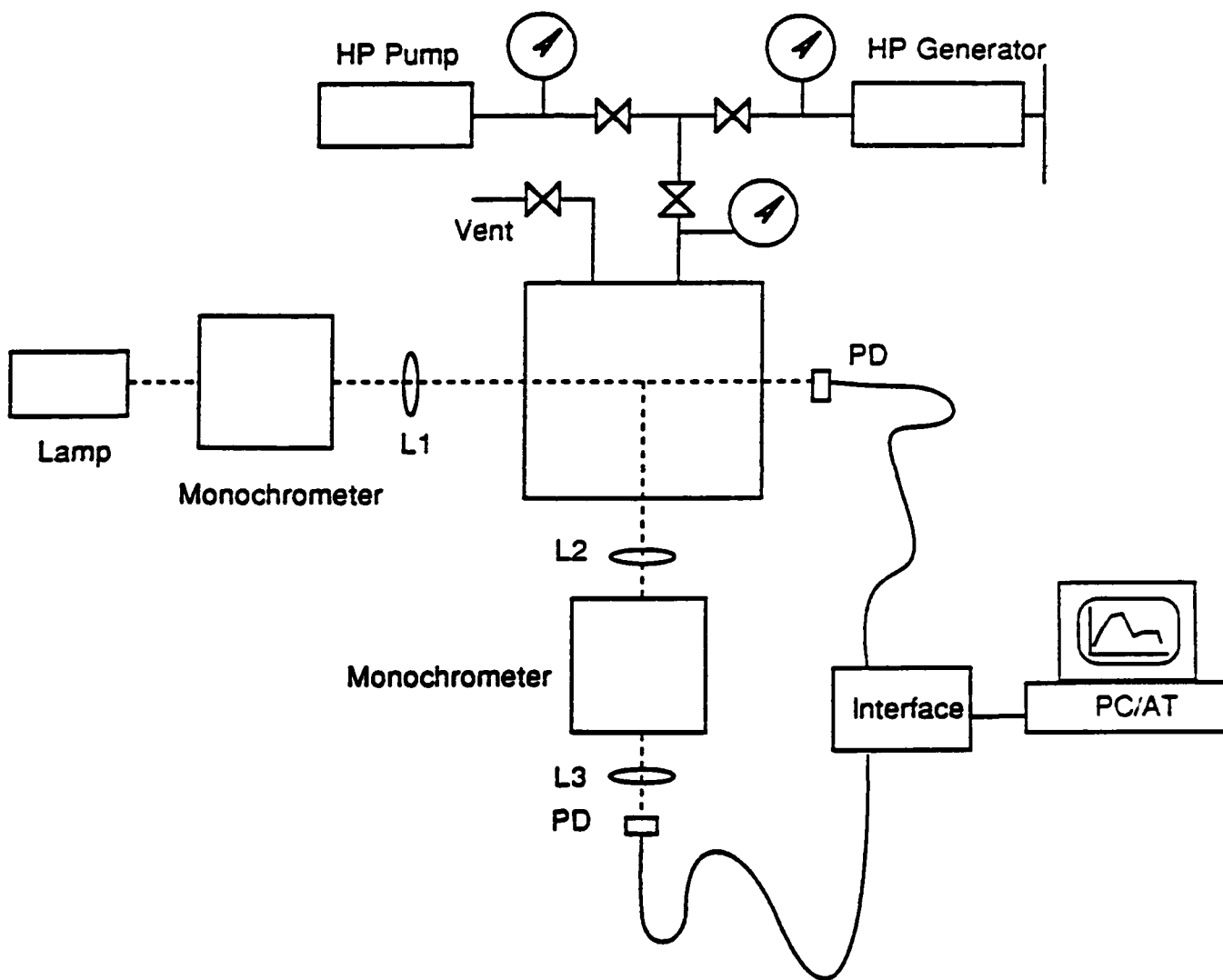
- Materials have not been available

Magnetic Sphere Rheometer

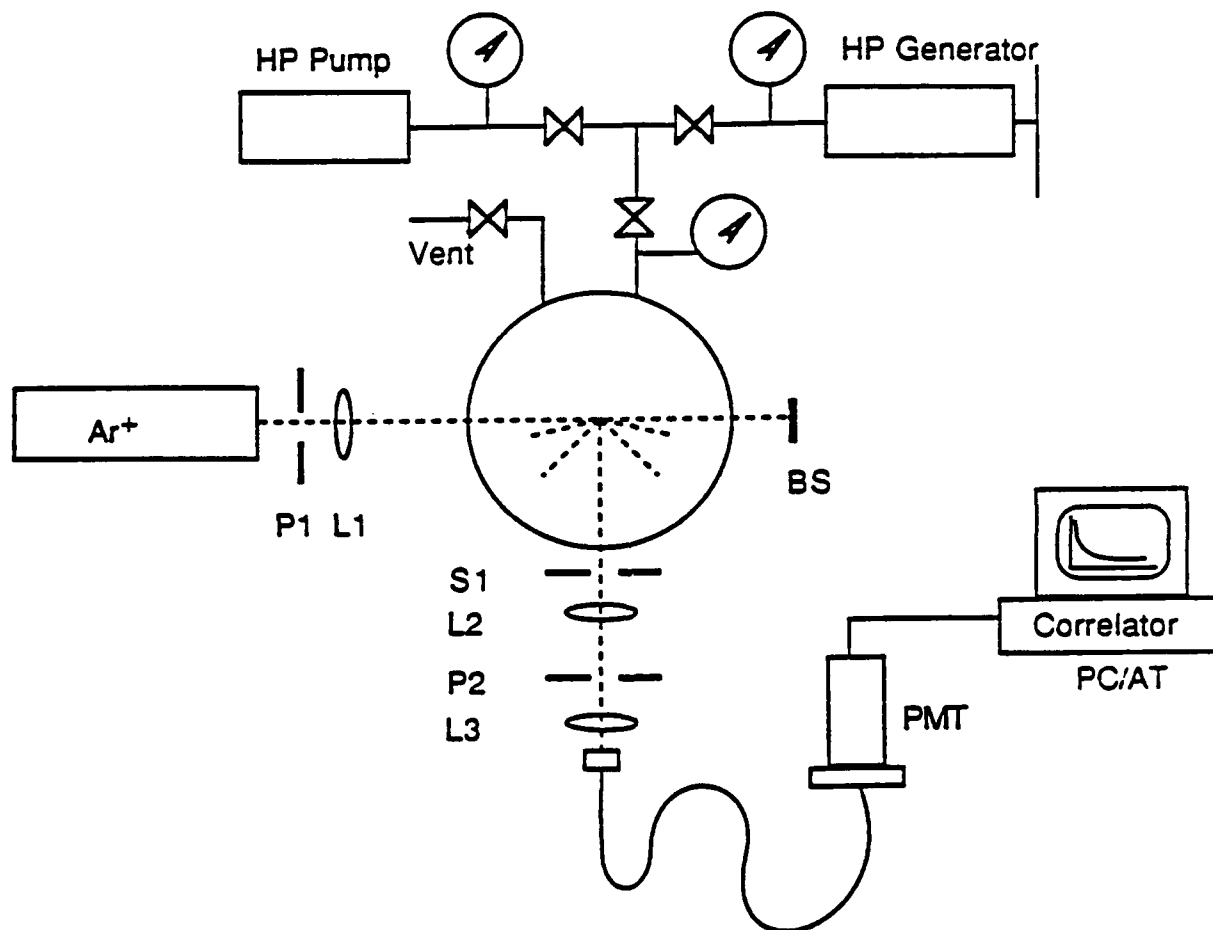


QD : Quadrant Detector; PA : Preamplifier; VG : Voltage Generator;
 CM : Current Meter; MC : Motor Controller; SM : Micro Stepping Motor;
 CO : Coil; MS : Magnetic Sphere; SC : Sample Cell; L : lense

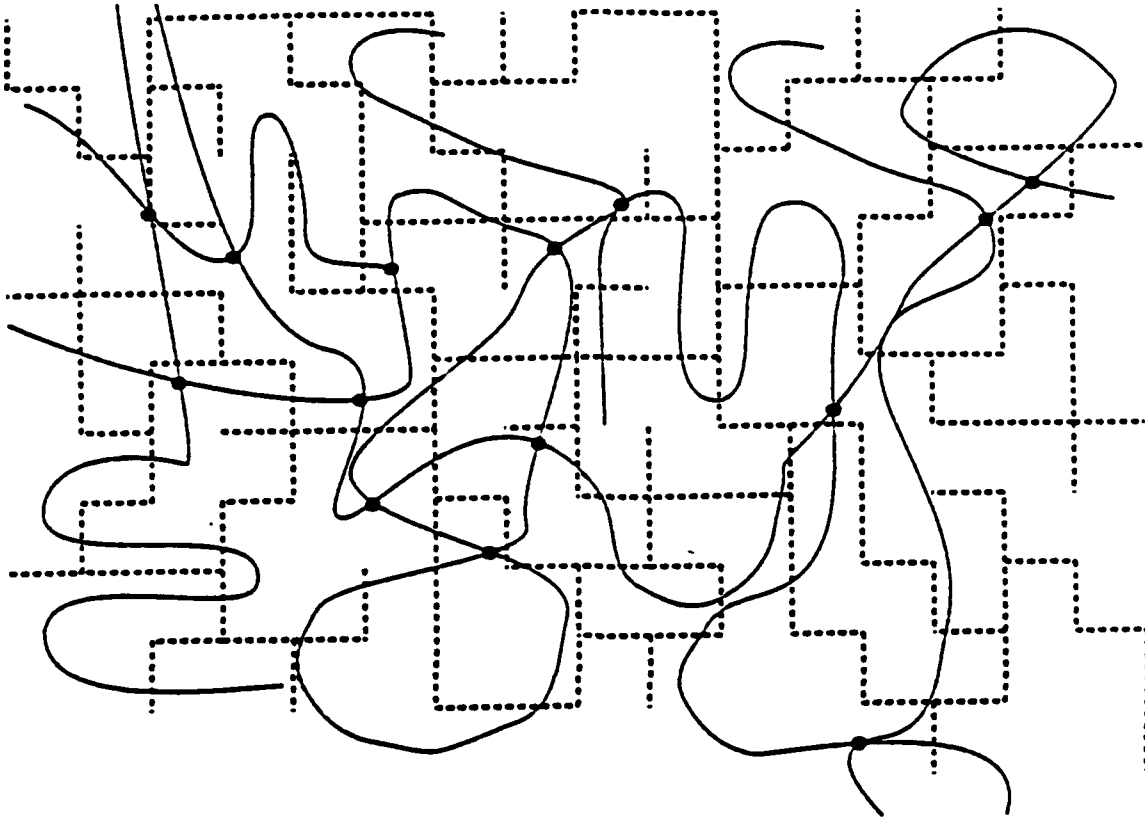
Supercritical Fluid Adsorption and Fluorescence Spectroscopy



Supercritical Fluid Dynamic Light Scattering



Interpenetrating polymer networks



- Mutually entangled networks or semi-IPN's
- Networks based on hydrophobic interactions
(hydrogen bonding, ion dipole, complexation)
- Single-phase dual network gels
- Inorganic-organic IPN's

Local dynamics by time-resolved fluorescence depolarization

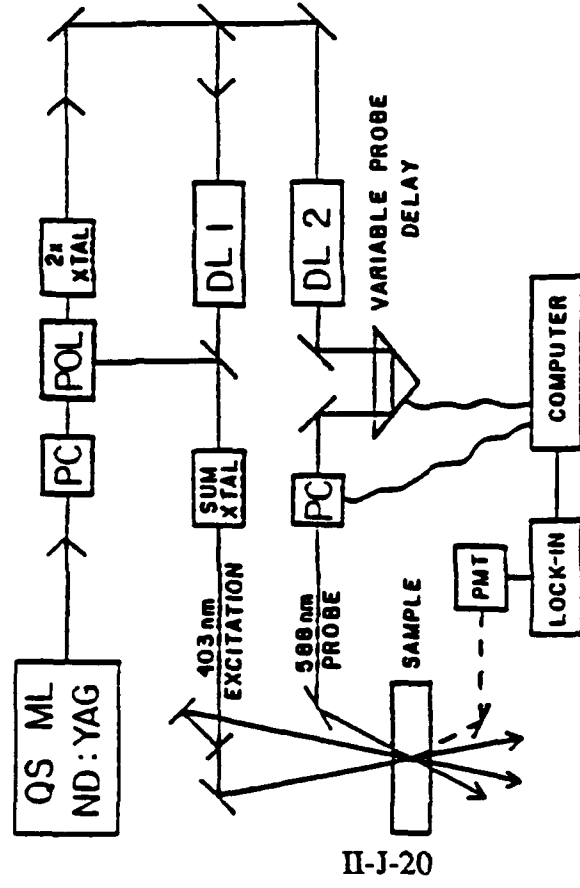


Figure 1. Q-switched, mode-locked Nd:YAG laser with two synchronously pumped dye lasers: PC, Pockels' cell; POL, polarizer with escape window; DL1, DL2, cavity-dumped dye lasers; PMT, photomultiplier tube.

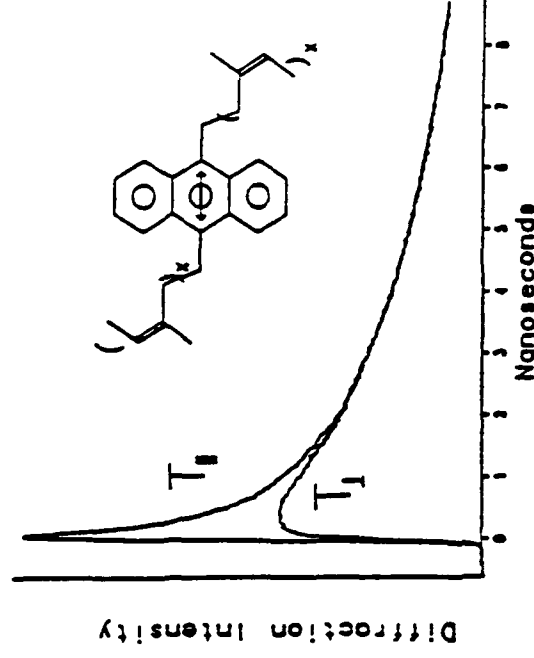


Figure 2. Transient grating decays for 9,10-bis(methylene)-anthracene-labeled polyisoprene in dilute hexane solution. T_1 and T_2 are the diffraction efficiencies of the grating for the probe beam polarized parallel and perpendicular to the excitation beams (see eq 2 and 3). The two curves are initially different because the excitation beams create an anisotropic orientational distribution of excited-state transition dipoles. As backbone motions occur, the transition dipoles randomize and the two curves coalesce. Both curves eventually decay due to the excited-state lifetime. The structure of the anthracene-labeled polyisoprene is also displayed, with the position of the transition dipole indicated by a double arrow. The correlation function obtained from these curves is shown in Figure 3.

in collaboration with M. Ediger (Wisconsin)

**VIRGINIA POLYTECHNIC INSTITUTE
AND STATE UNIVERSITY**

Professor James E. McGrath

DARPA REVIEW

January 15, 1992

700°F Amorphous or Semi-Crystalline Polymeric Matrix Resins and Structural Adhesives

James E. McGrath
Virginia Polytechnic Institute and State University
Department of Chemistry
Blacksburg, VA 24061-0212
Phone: (703) 231-5976
Fax: (703) 231-8517

**DARPA/ARO Support
Contract No. DAAL03-91-G-0140
May 1, 1991 to Present**

OBJECTIVES

**Identify Organic Material
Systems and Processes for 700°F
Applications**

- **Monomer and Polymer
Synthesis**
- **Processing** — *control, storage, etc.*
- **Testing Methodologies**

**Knowledge/Technology Transfer
to**

- **Users**
- **Suppliers**
- **DOD Agencies**

OUTLINE

- Progress Report on Monomer/
Polymer/Processing/
Characterization

Potential Producers

- GE C.R.C.
- Maxdem

Characterization

- Foster-Miller
- Lockheed

Applications

- GE Aircraft Engines
- Lockheed - *Replace Ti in F-2 & F-16*
- High Performance Turbines (?)

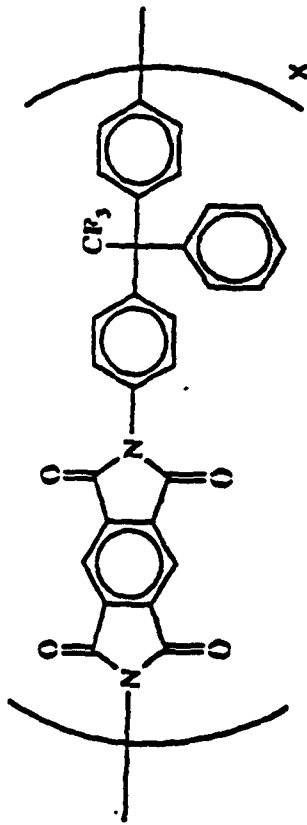
BACKGROUND

- **DARPA/AFOSR Polymer Blends Project**
 - Polyimide/PBI Systems
 - Hoechst Celanese/Lockheed, U. Mass, Virginia Tech
- **Achievements**
 - Attractive properties identified with PI/PBI blends
 - Fluorinated polyimides showed very good stability at 650°F (1000 hrs)
- **Problems**
 - PBI long term thermoxidative stability
 - Polyimides studied had Tg values <700°F

INTRODUCTION

PMDA-3F DIAMINE POLYIMIDE

of which
assembly
only available
originally
#15, 1977, No. 4
T. J. Alston, George
D. Weber



Tg = 440°C - 450°C
processing temperatures of 425°C to 475°C were needed to
obtain Tg's > 400°C

W. B. Alston and R. F. Gratz, "Structure-to-Glass Transition Temperature Relationships in High Temperature Stable Condensation Polyimides" in Recent Advances in Polyimide Science and Technology, edited by W. D. Weber and M. R. Gupta, 1987.

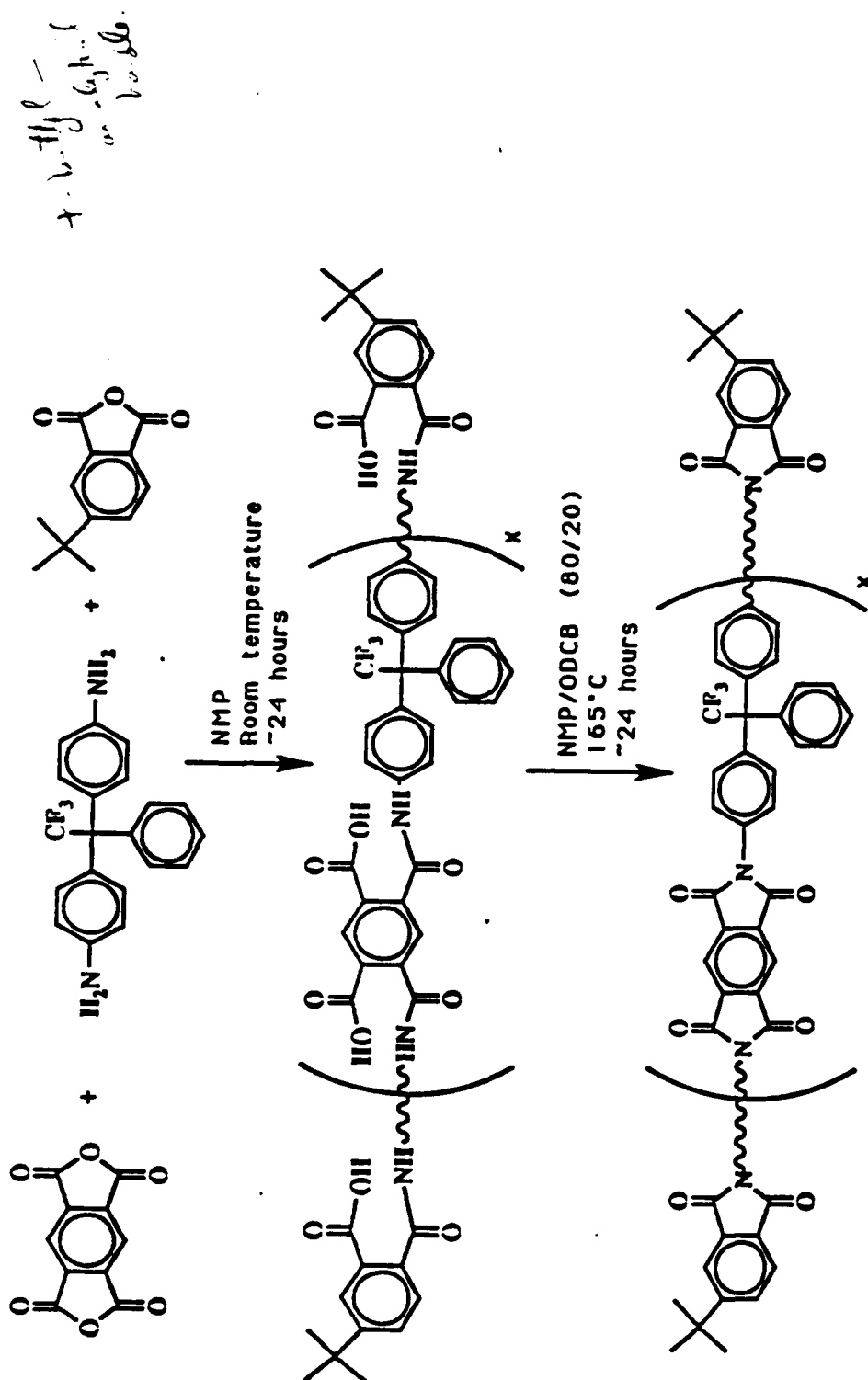
OBJECTIVE

**DEVELOP POLYMERS OF IMPROVED PROCESSABILITY
AND THERMOOXIDATIVE STABILITY FOR HIGH
TEMPERATURE APPLICATIONS**

METHODS OF IMPROVING PROCESSABILITY

- FLEXIBLE LINKAGES**
- MOLECULAR WEIGHT CONTROL**
- NONREACTIVE ENDGROUPS**
- SOLUTION IMIDIZATION**

SYNTHESIS OF "3F" POLYIMIDES



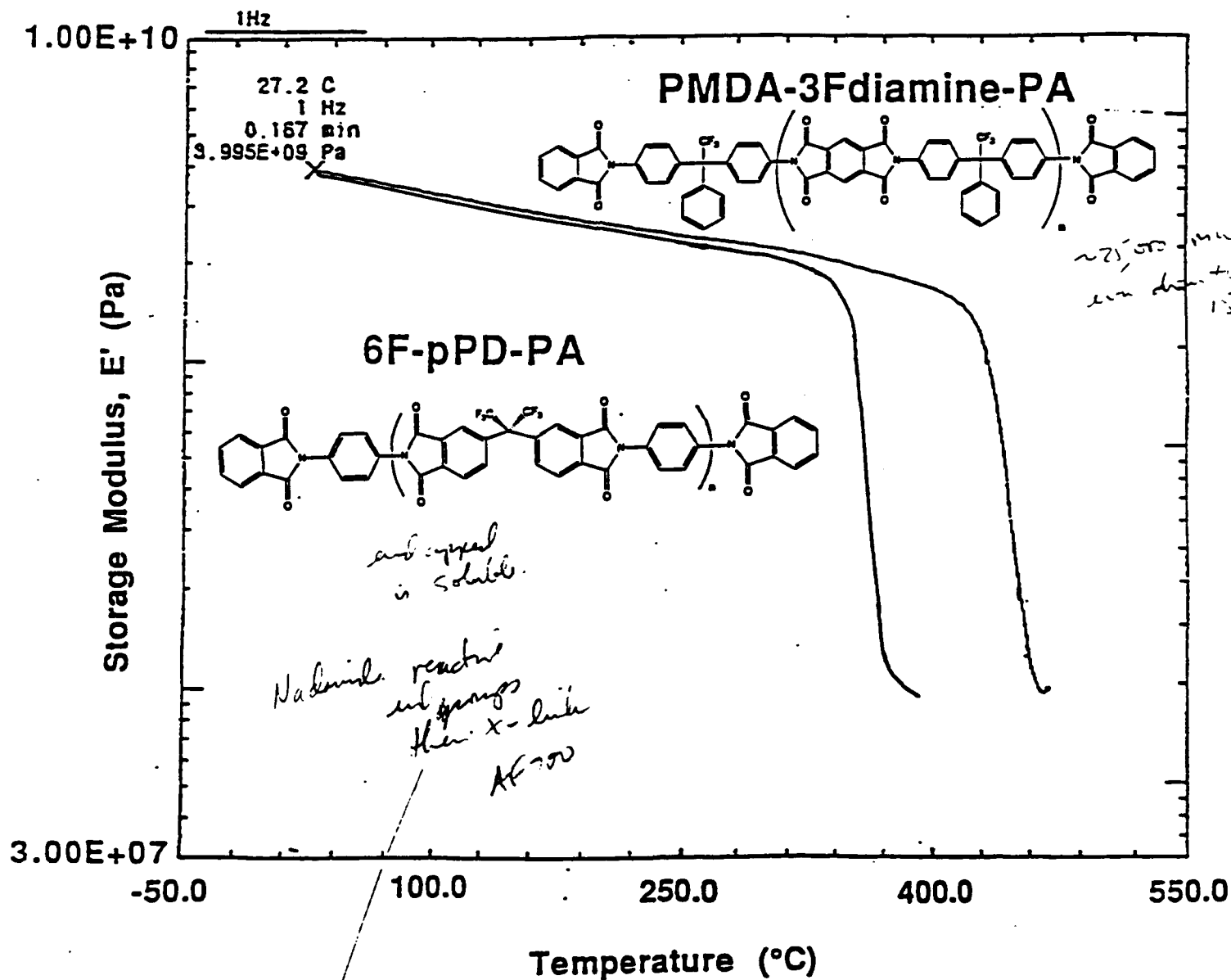
"3F" POLYIMIDE HOMOPOLYMERS

	<u><Mn></u> <u>Theor.</u>	<u><Mn></u> <u>n.m.r.</u>	<u>[η]*</u> <u>dl/g</u>	<u>Solubility</u>		<u>Tg</u> <u>°C</u>	<u>5%</u> <u>wt. loss(°C)</u>
				<u>NMP</u>	<u>CHCl₃</u>		
PMDA-3FDIAMINE-t butyl PA	10,000	10,200	0.32	S	----	---	-----
	20,000	18500	0.47	S	MS	422	543
	30,000	33,600	0.65	S	----	432	541
BPDA-3FDIAMINE-PA	30,000	-----	0.44	S	S	350	536
6FDA-3FDIAMINE-PA	30,000	-----	0.36	S	S	314	527

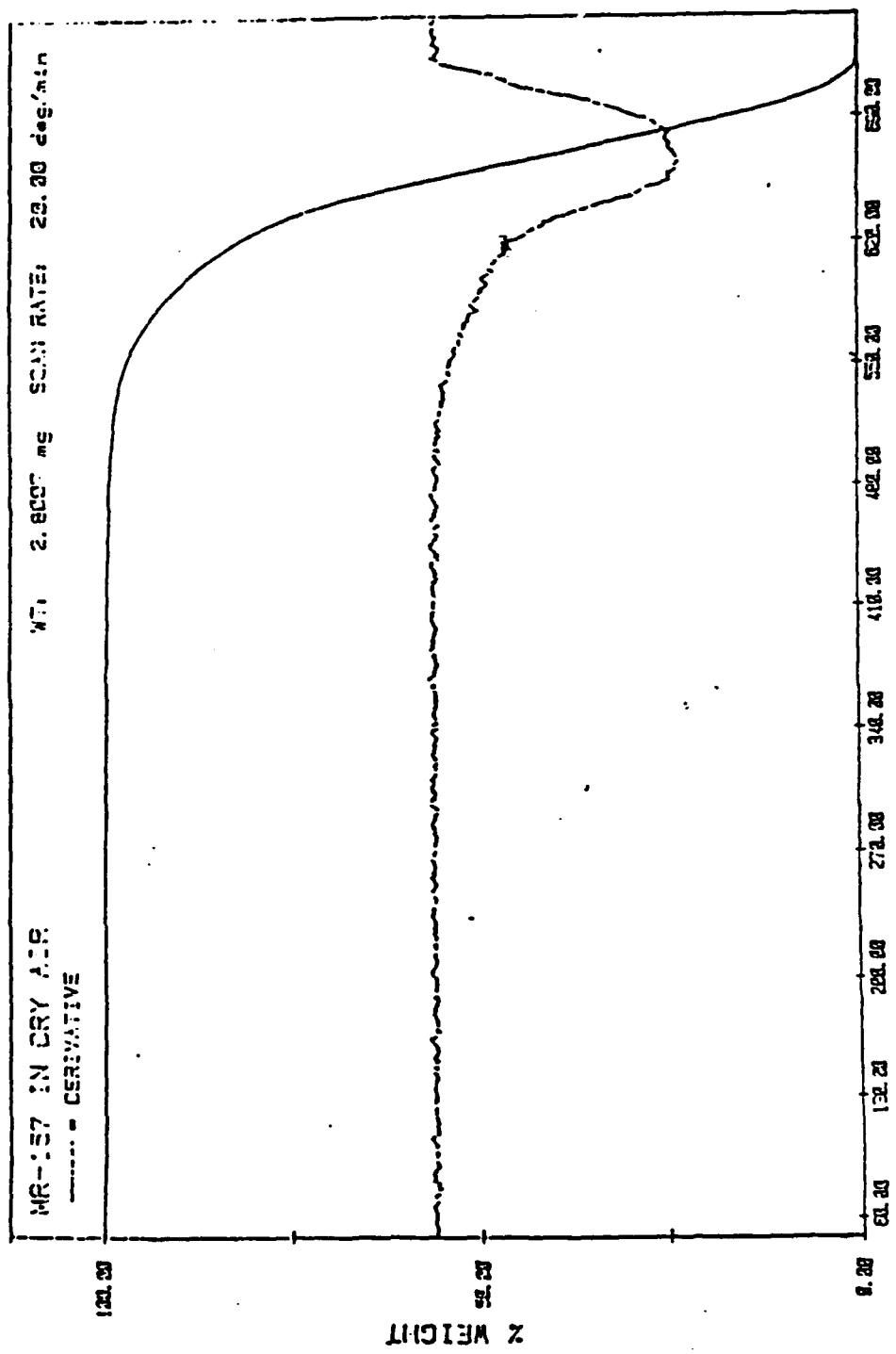
A soluble system

* Intrinsic viscosities were conducted in NMP at 25°C.

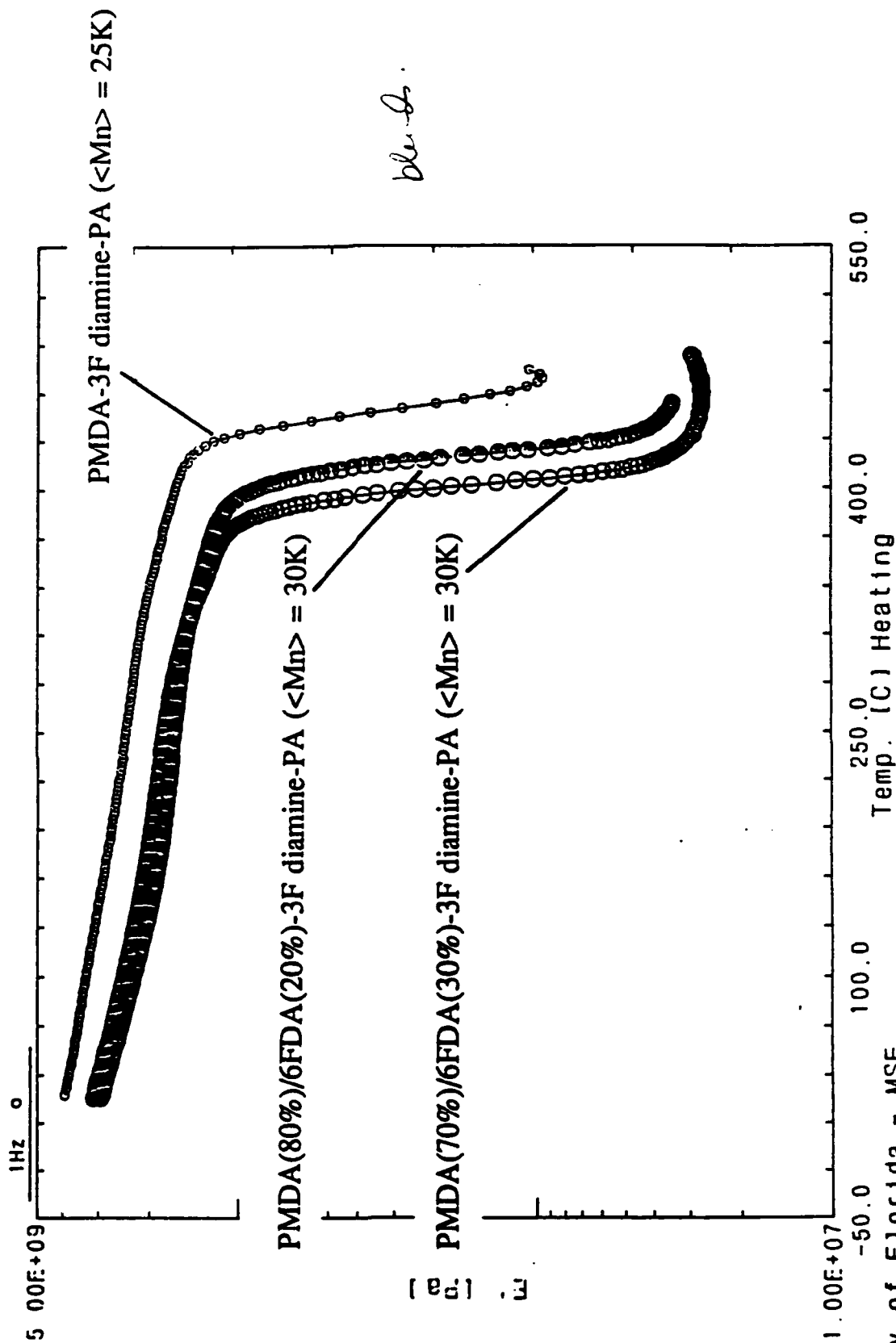
Stiffness-Temperature Behavior of New PMDA-3Fdiamine-PA Polyimides Compared with the State of the Art 6F-pPD-PA Polyimides



DYNAMIC TGA THERMOGRAM OF 3FDAM-PMDA-PA (<Mn> = 25K)



Storage Modulus Versus Temperature Plots of the 3F diamine Containing Polyimide Homopolymers and Copolymers

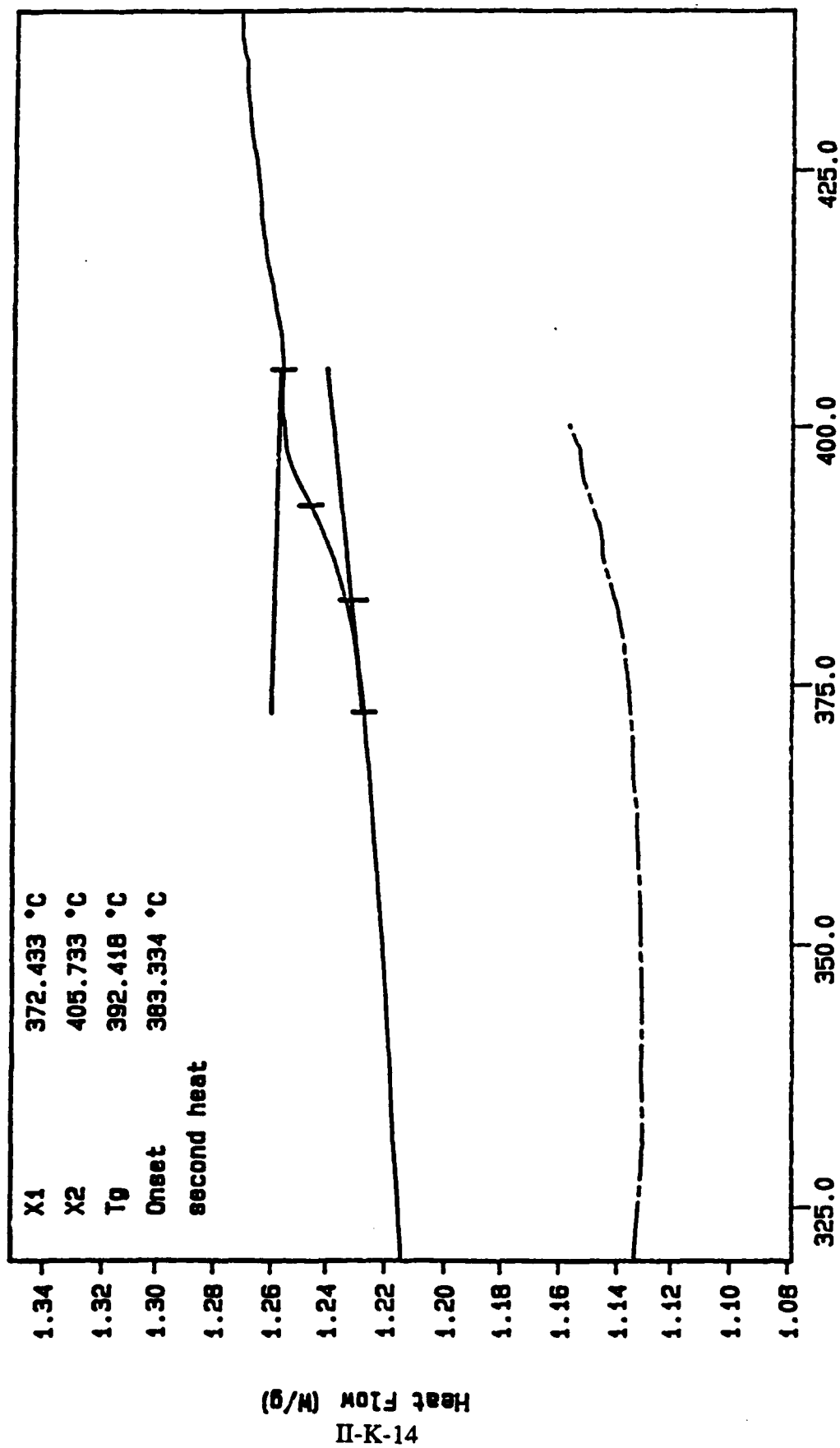


Curve 1: DSC7

File Info: nr207 Wed Jan 08 21:28:11 1992

Sample Weight: 18.530 mg

Sample ID: (78)8f86(72)25fd1am1he-pa1nr207.30K9

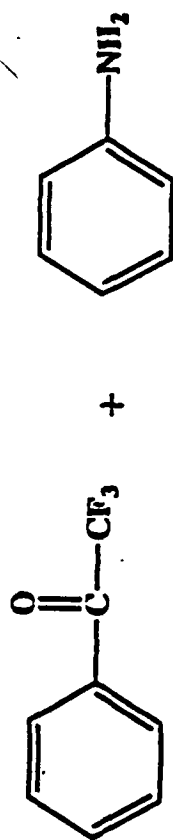


TEMP: 300.0 °C TIME: 2.0 min RATE: 10.0 °/min

m.e. rogers
PERKIN-ELMER
7 Series Thermal Analysis System
Wed Jan 08 21:46:54 1992

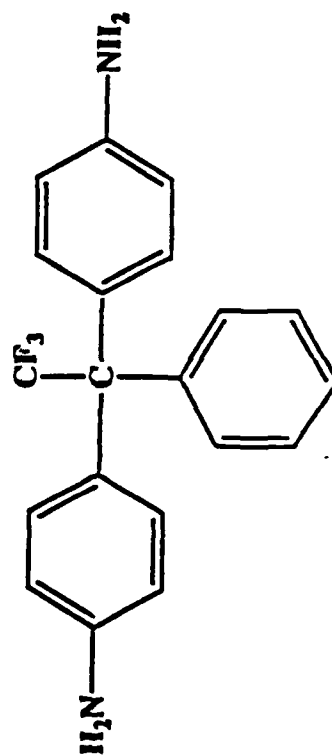
MAJOR PROCESS IMPROVEMENTS
HAVE BEEN ACHIEVED

3F Diamine Synthesis



Aniline Hydrochloride
reflux, 24 hours

Purified yield ~80%

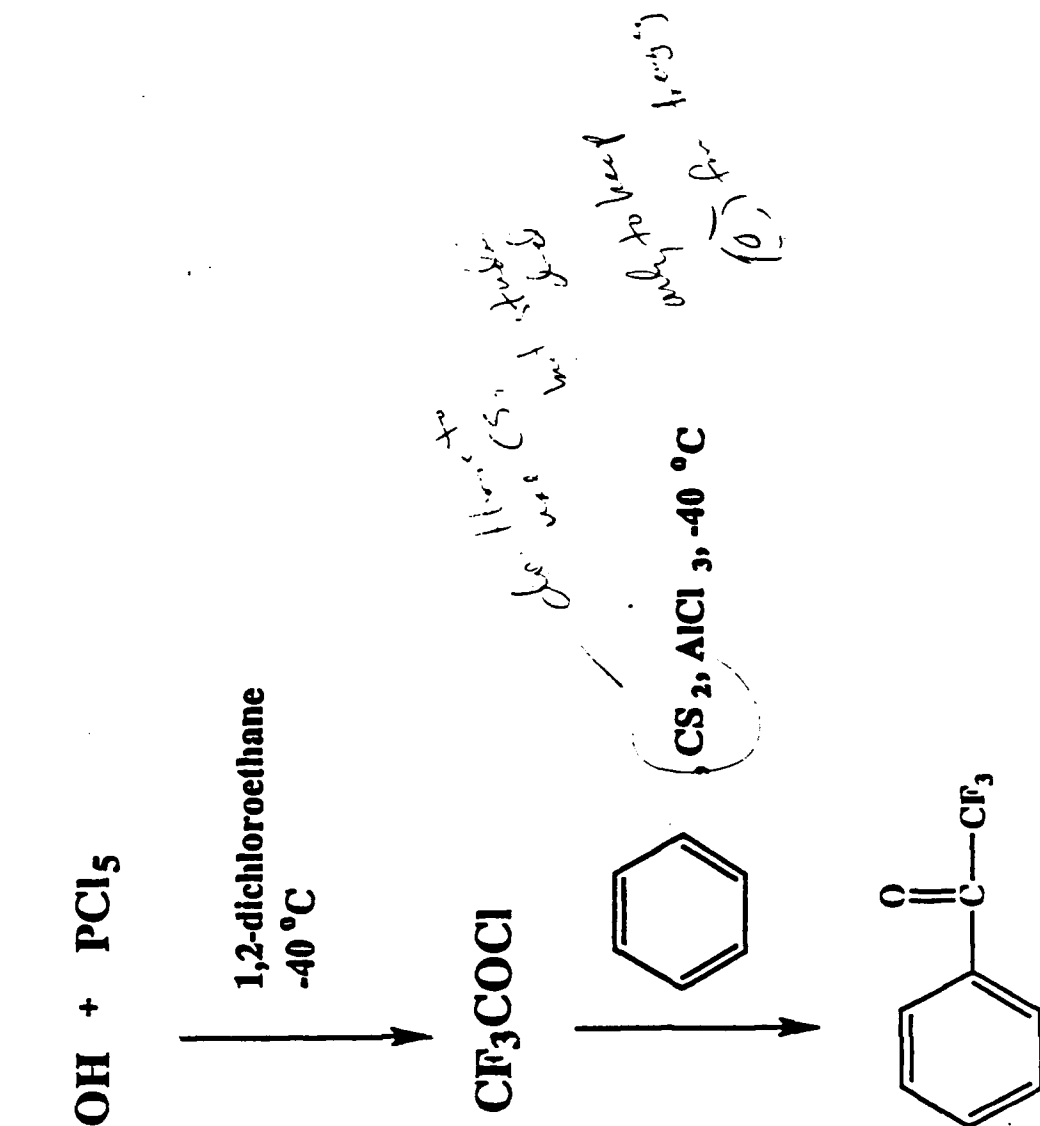


Product is very pure

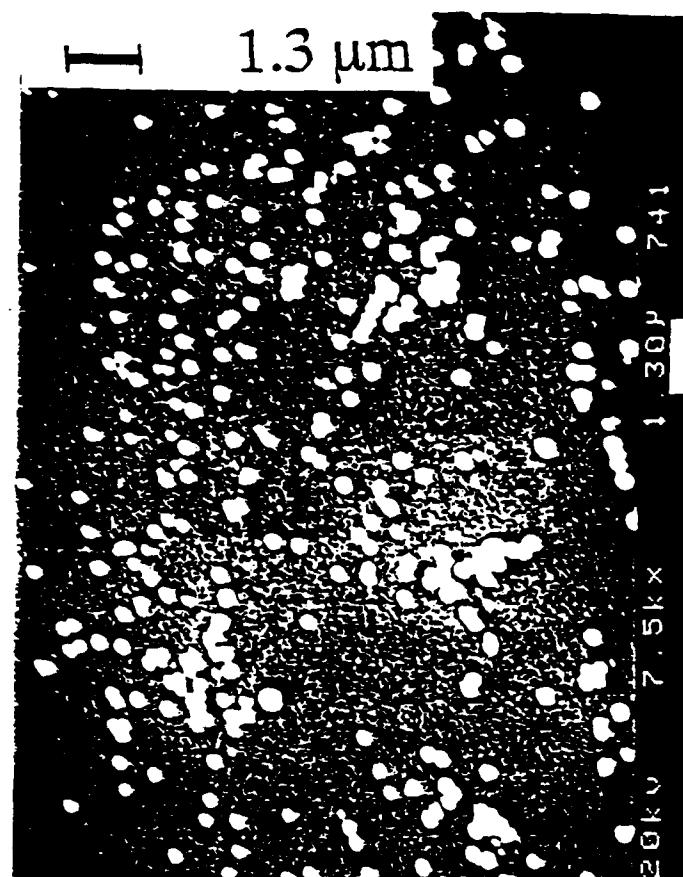
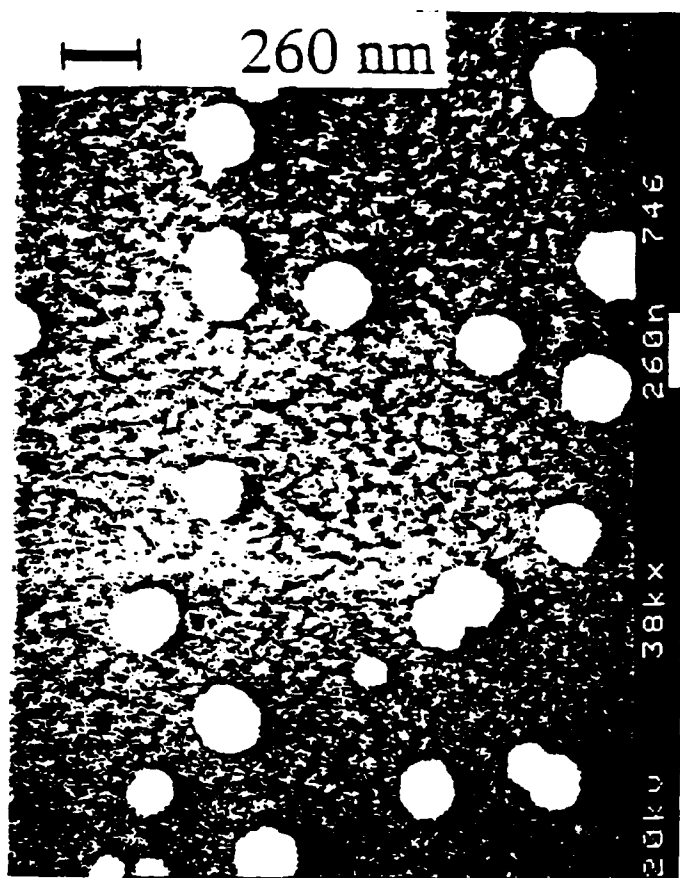
II-K-15

KEY INTERMEDIATE SUCCESSFULLY PREPARED
WITH INDUSTRIALLY AVAILABLE REACTANTS

Synthesis of Trifluoroacetophenone



Processing



PMDA - 3F Diamine - PA Particles
from a 4 wt% solution in NMP/H₂O (93/7)

Cooling from 90 °C to 20 °C at 23.3 °C/min
under 1100 RPM stirring rate

WHY FINE PARTICLES?

- Processing of new polymers with very high transition temperatures

Small, well-packed particles may allow for melt consolidation at lower temperatures or in shorter time cycles.

- New processing methods for mixed particulate composites

Homogeneity of dry blends improves as particle size decreases. Small particle dry blends of polymer/metal or polymer/ceramic materials allows direct molding fabrication.

- Elimination of toxic solvents in composite processing

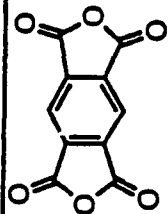
POLYIMIDE BUILDING BLOCKS



2,2-BIS[4-(4-AMINOPHENOXY)PHENYL]-
HEXAFLUOROPROPANE

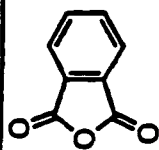
BDAF

II-K-19



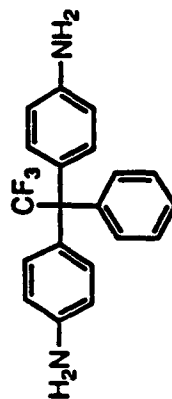
PYROMELLITIC DIANHYDRIDE

PMDA



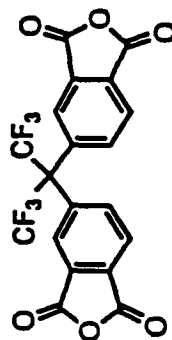
PHTHALIC ANHYDRIDE

PA



1,1,1-BIS(4-AMINOPHENYL)-1-PHENYL-
2,2,2-TRIFLUOROETHANE

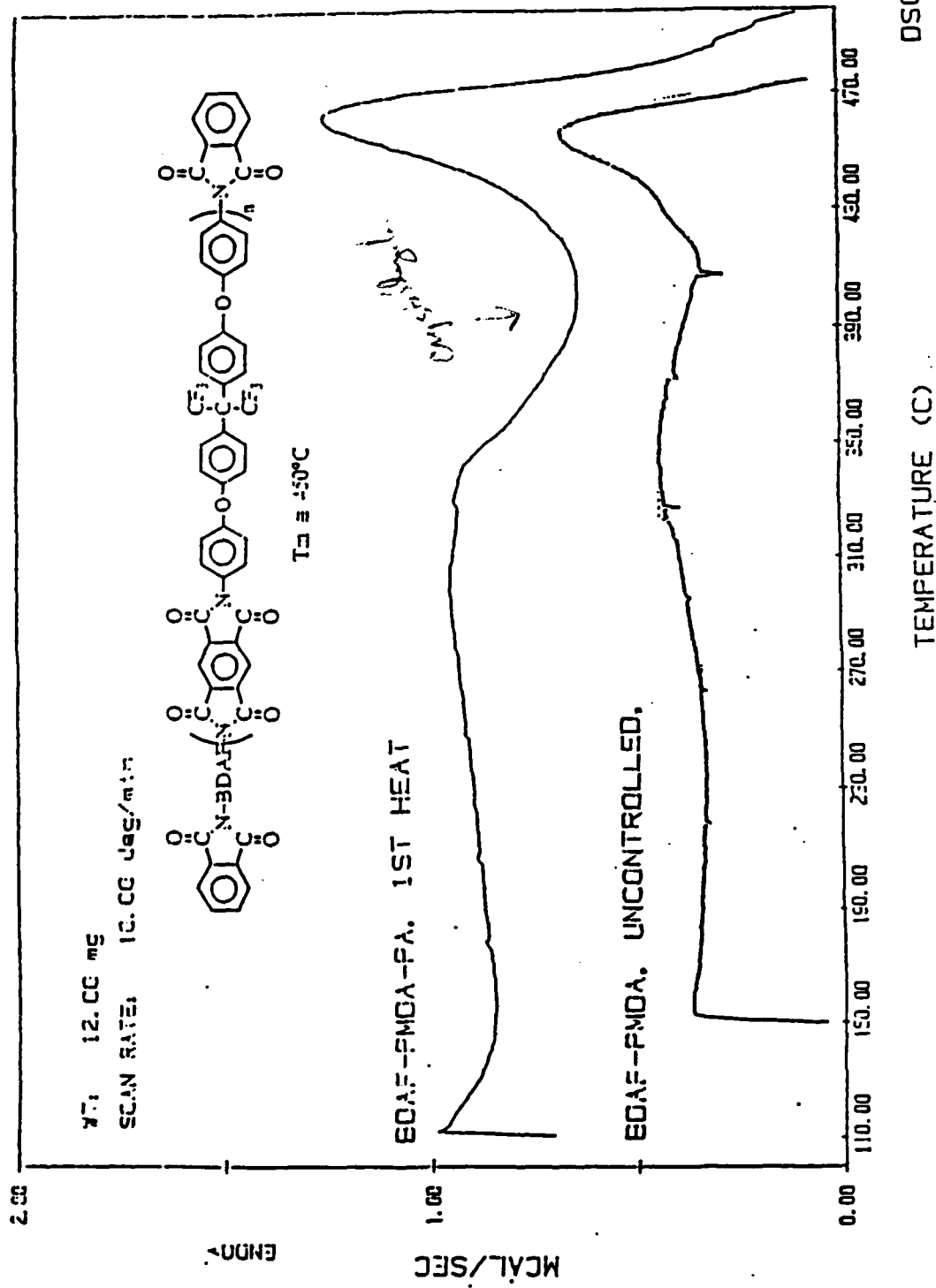
3FDA



HEXAFLUOROISOPROPYLIDENE-
2,2-BISPHTHALIC ACID ANHYDRIDE

6FDA

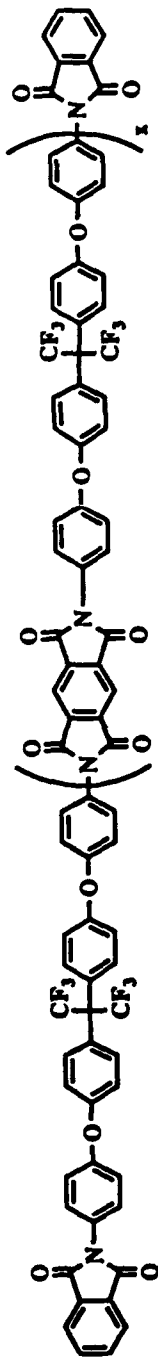
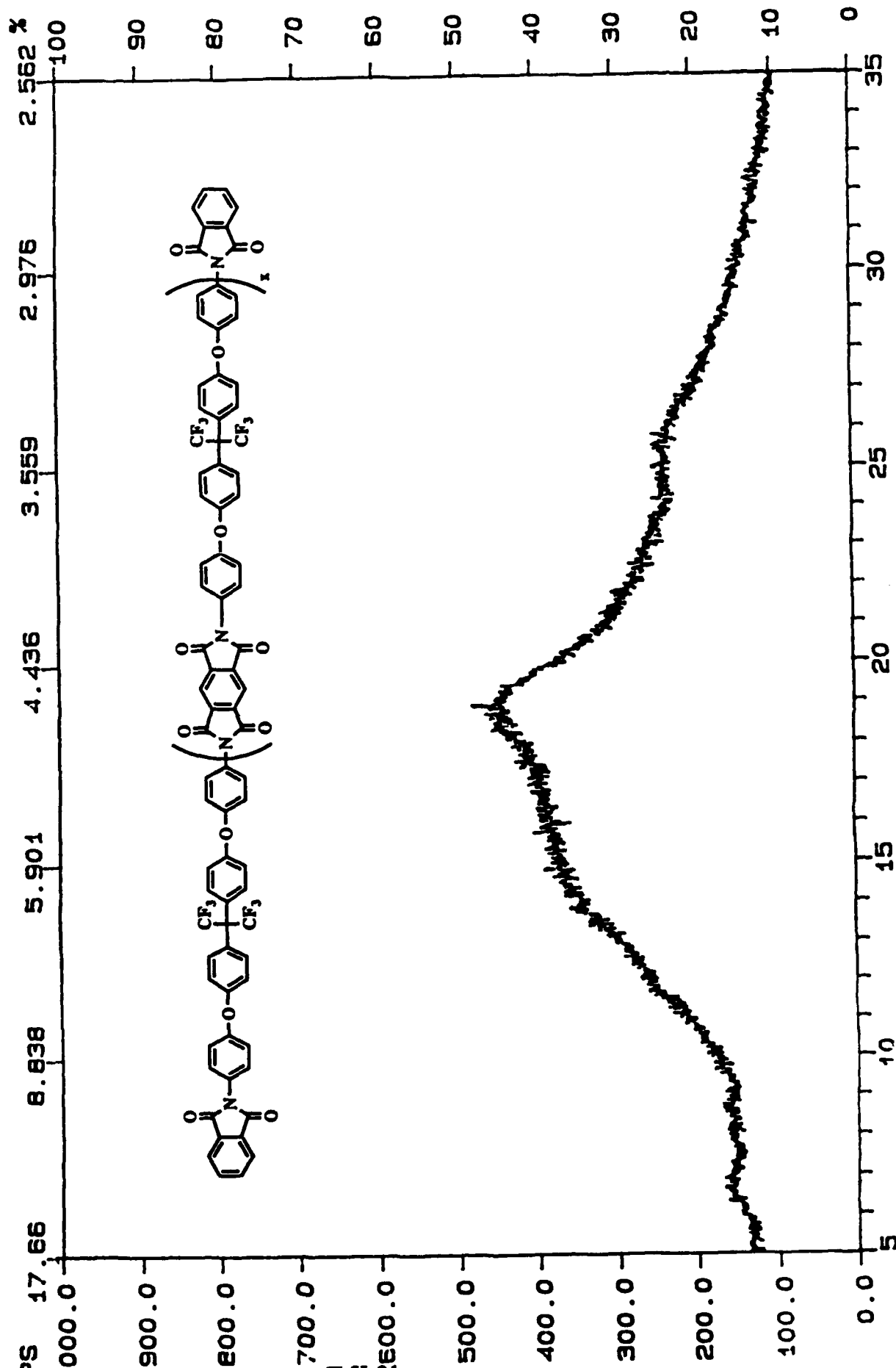
DSC SCAN OF BDAF-PMDA-PA



II-K-20

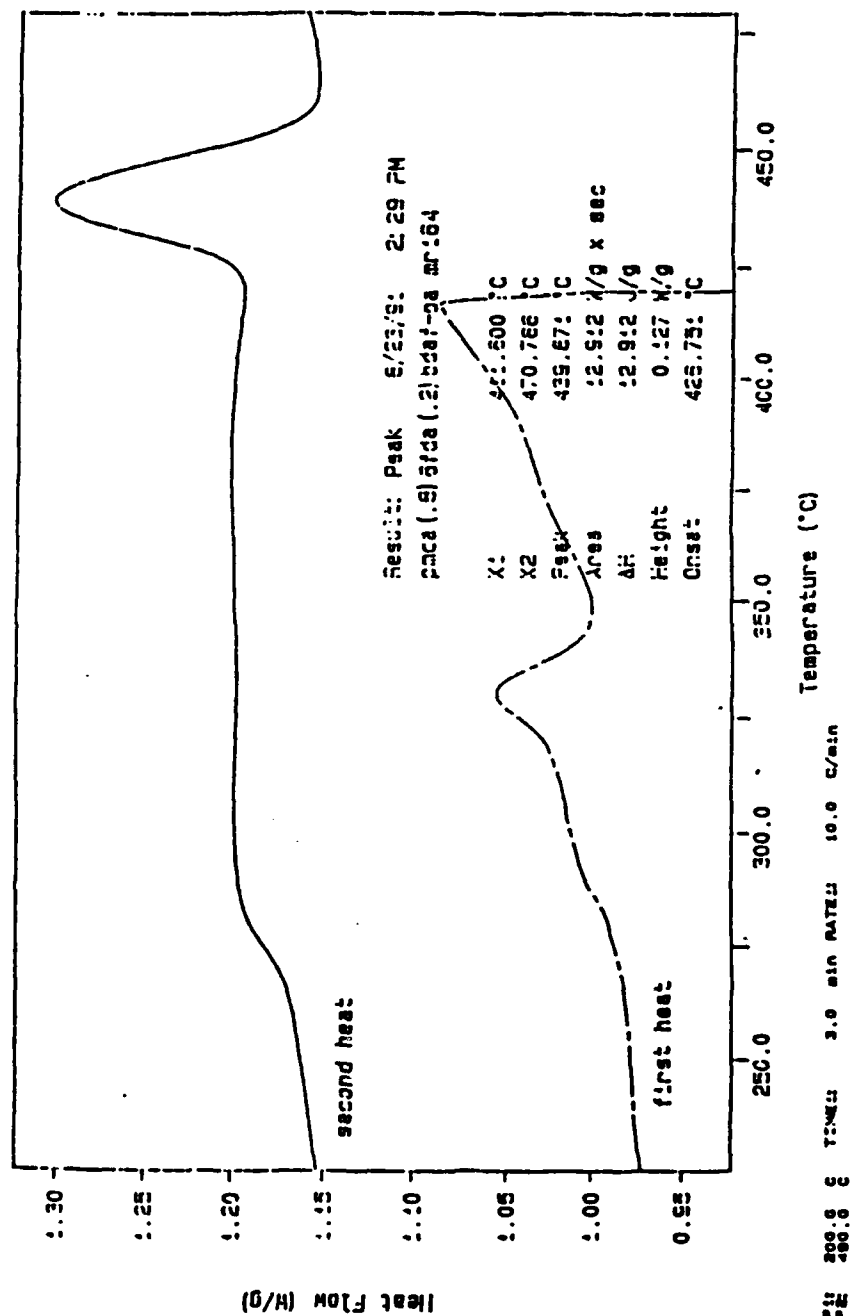
VIRGINIA TECH

WAXS of PMDA-4-BDAF-PA POLYIMIDE



File 10-132
 II-K-21

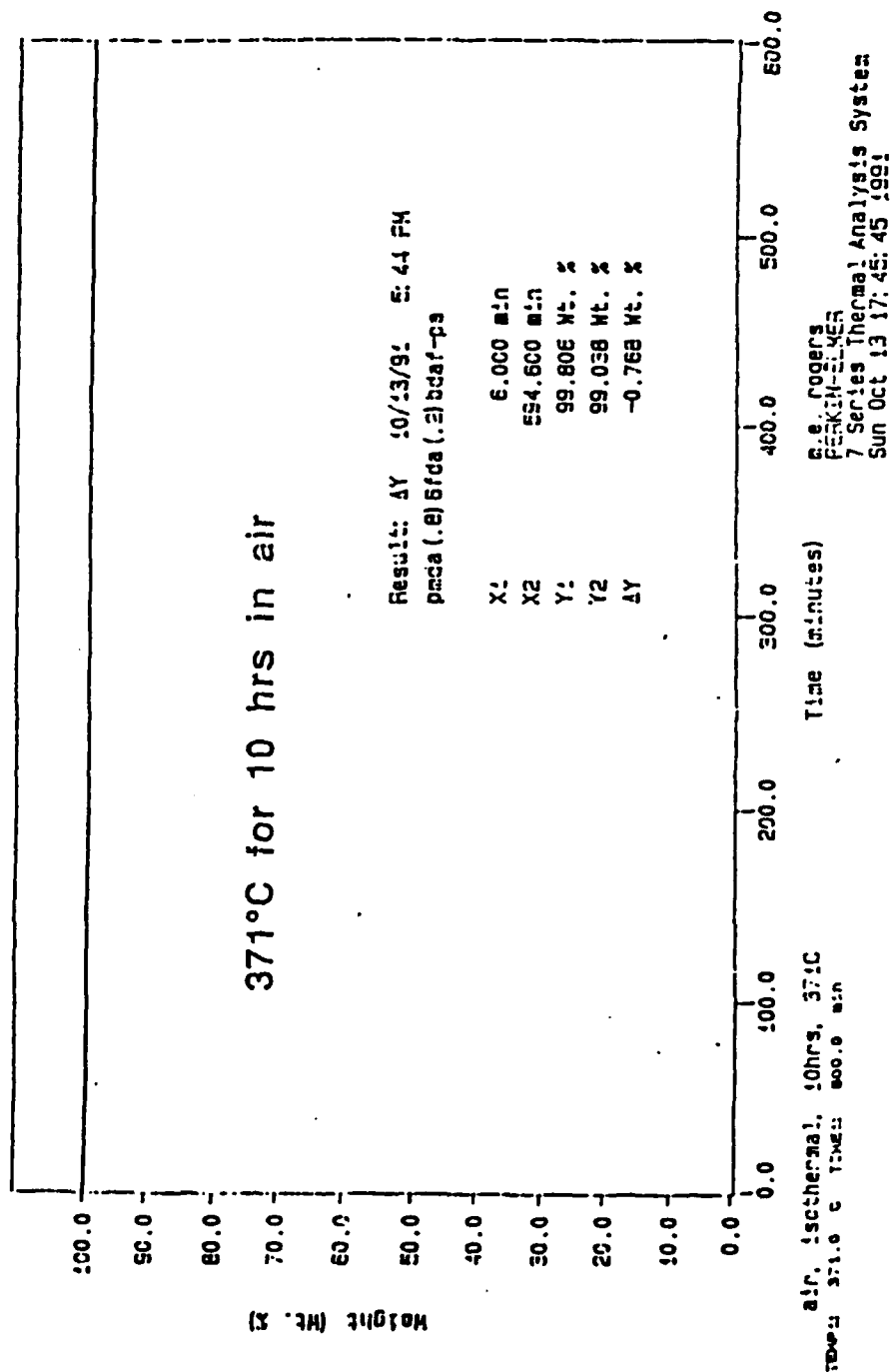
DSC SCAN OF BDAF-20%6FDA-80% PMDA-PA



VIRGINIA TECH

II-K-22

ISOTHERMAL TGA THERMOGRAM OF BDAF-20%6FDA-80%PMDA-PA (<Mn> = 30K)



Soluble Polybenzoxazoles via Acid-Catalyzed Solution Cyclization Techniques

W. A. Joseph, R. Mercier, H. Grubbs, A. Brennan and J. E. McGrath

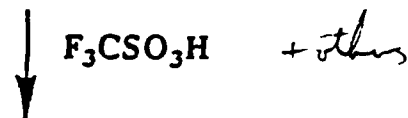
II-K-24

Department of Chemistry
NSF Science and Technology Center for High Performance Polymeric Adhesives and
Composites

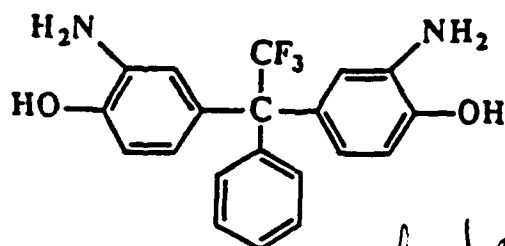
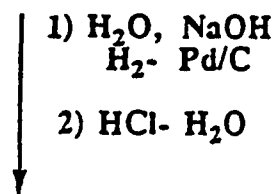
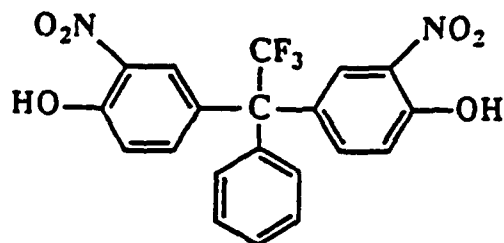
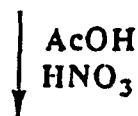
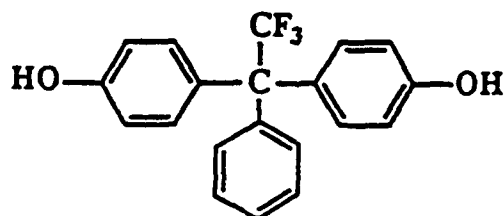
Virginia Polytechnic Institute and State University
Blacksburg, VA 24061

DARPA/ARO

3F-Bisaminophenol Synthesis



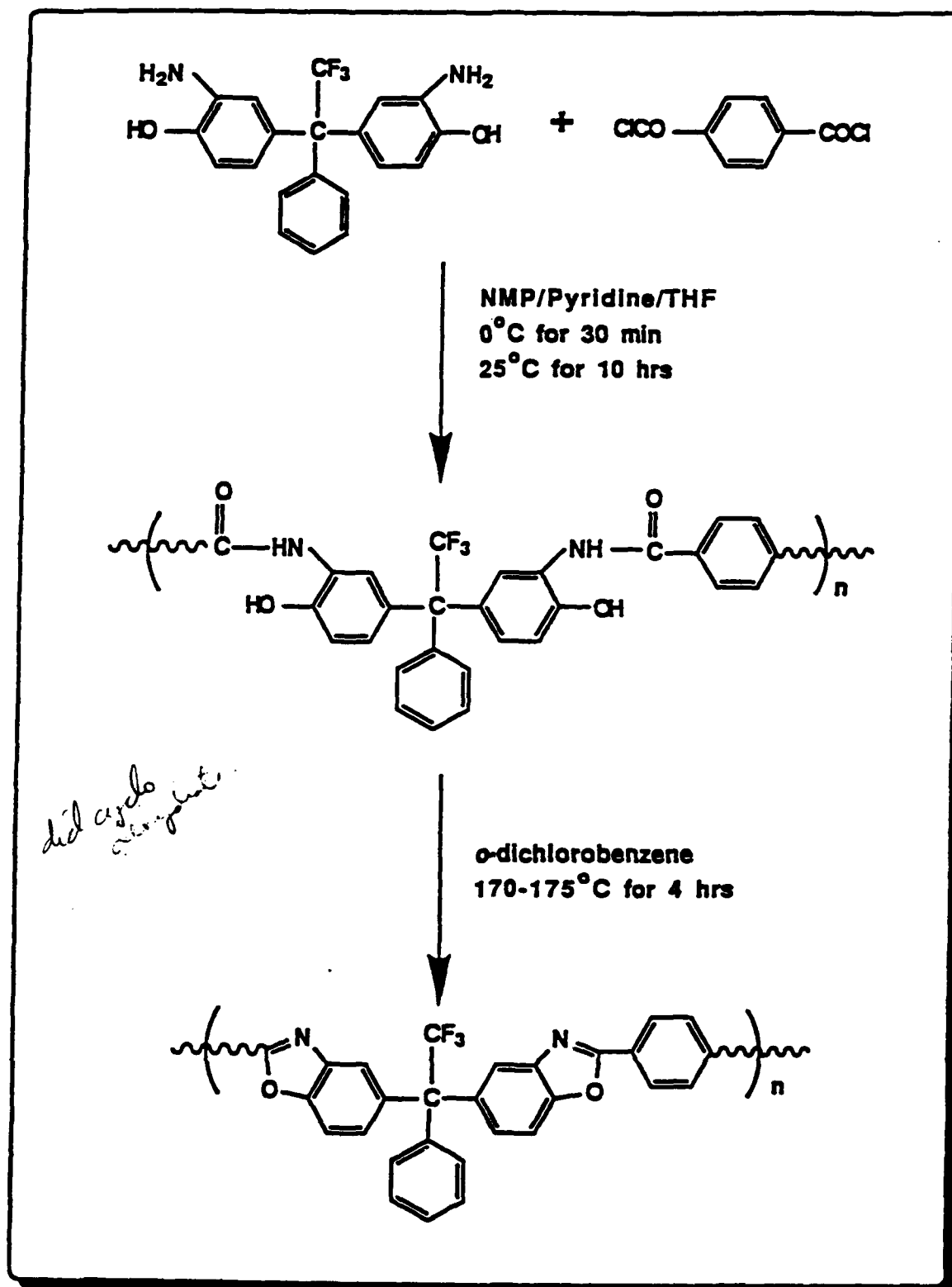
*Source
containing
material*



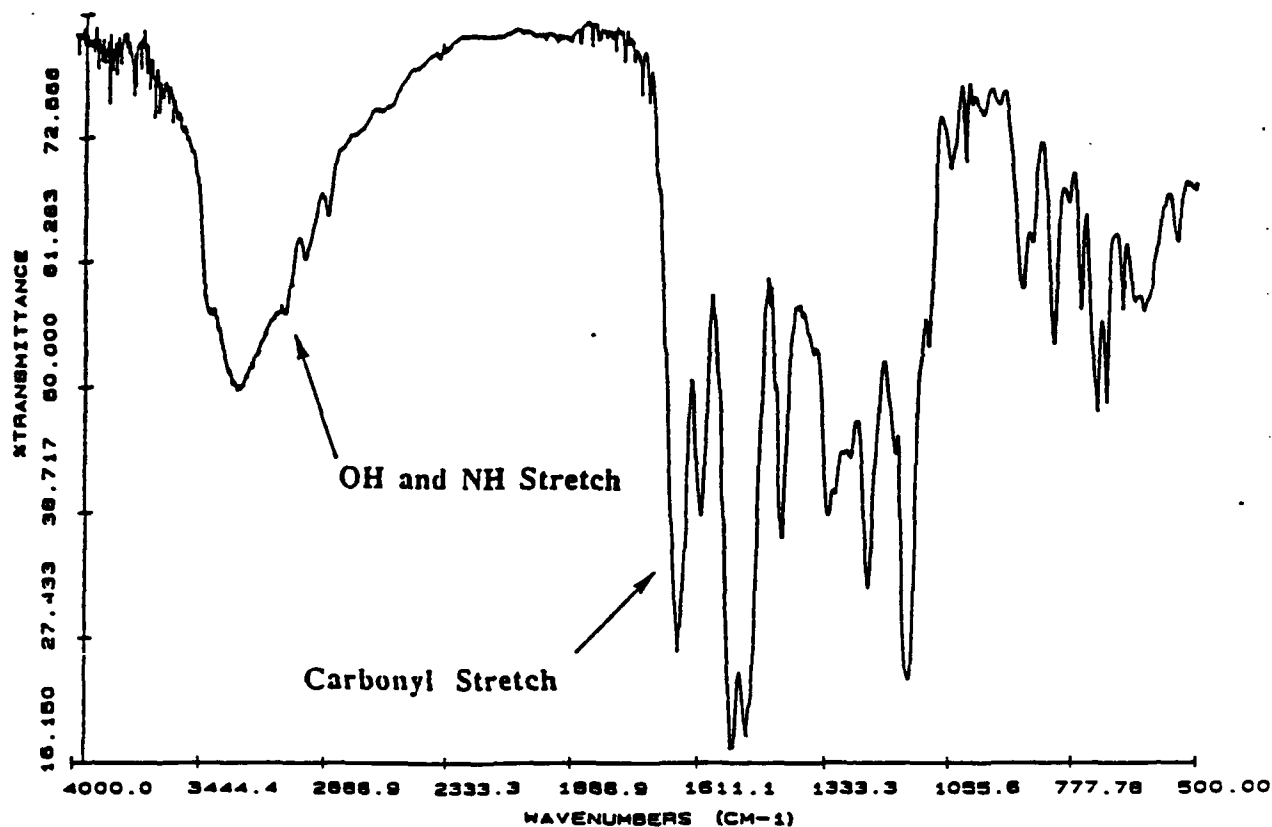
II-K-25

phenyl at 4-position

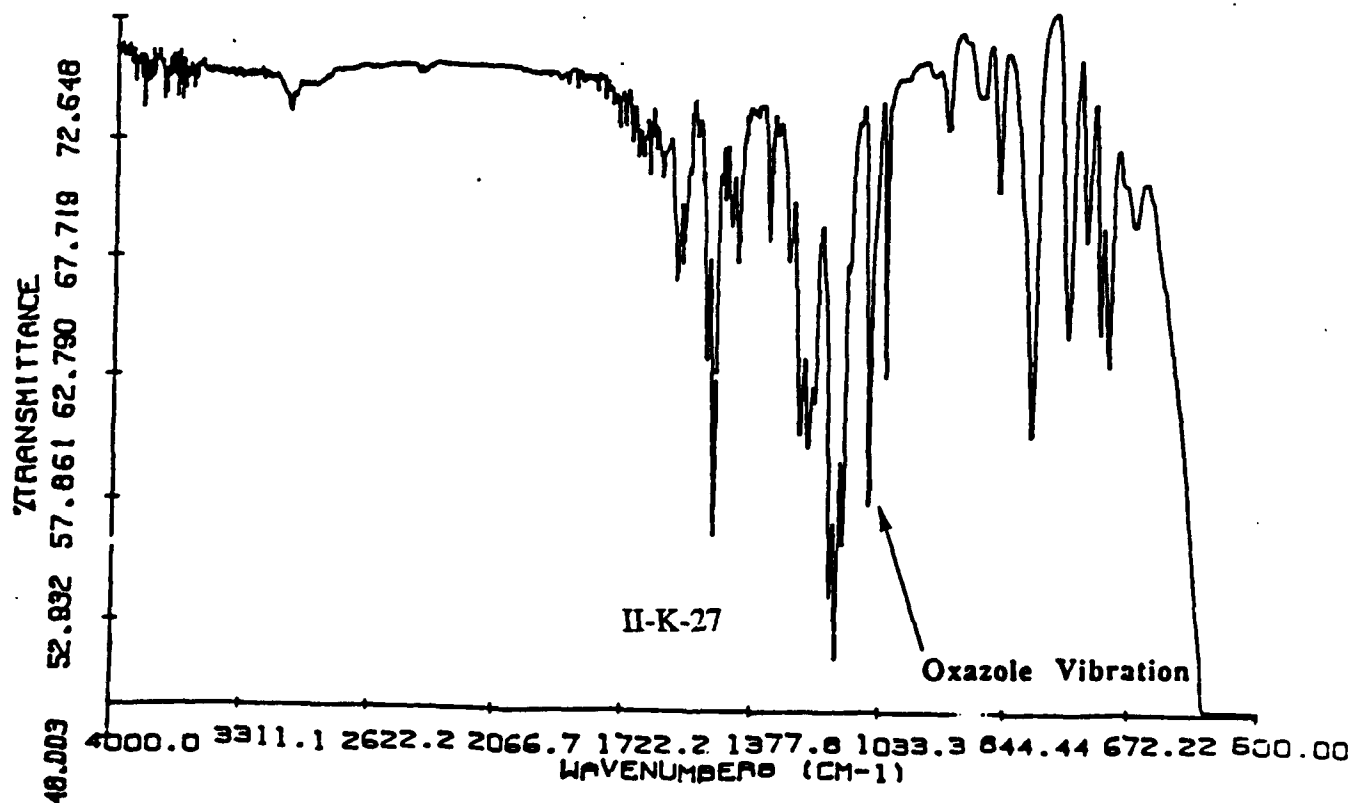
Polybenzoxazole Polymerization

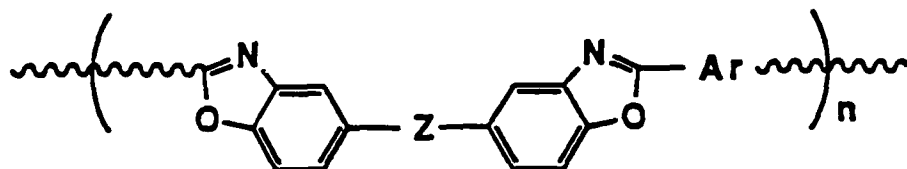


Infrared Spectrum of 3F-bAP-TC PHA



Infrared Spectrum of 3F-bAP-TC PBO





Solution Cyclized

Polymer Structure		PBO $[\eta]^1$	Tg	5% Wt. Loss
Z	Ar	(dl/g)	(°C)	(°C)
C(CF ₃) ₂		0.46	361	531
C(CF ₃)(Ph)		0.23	369	536
C(CH ₃) ₂		--- ²	--- ³	385

Thermally Cyclized

Polymer Structure		PHA $[\eta]^4$	Tg	5% Wt. Loss
Z	Ar	(dl/g)	(°C)	(°C)
C(CF ₃) ₂		0.38	300	536
C(CF ₃) ₂		0.46	363	531
C(CF ₃)(Ph)		0.31	355	535
C(CH ₃) ₂		0.67	313 ⁵	492

1 Intrinsic done in *m*-cresol at 25°C

2 Precipitates during cyclization

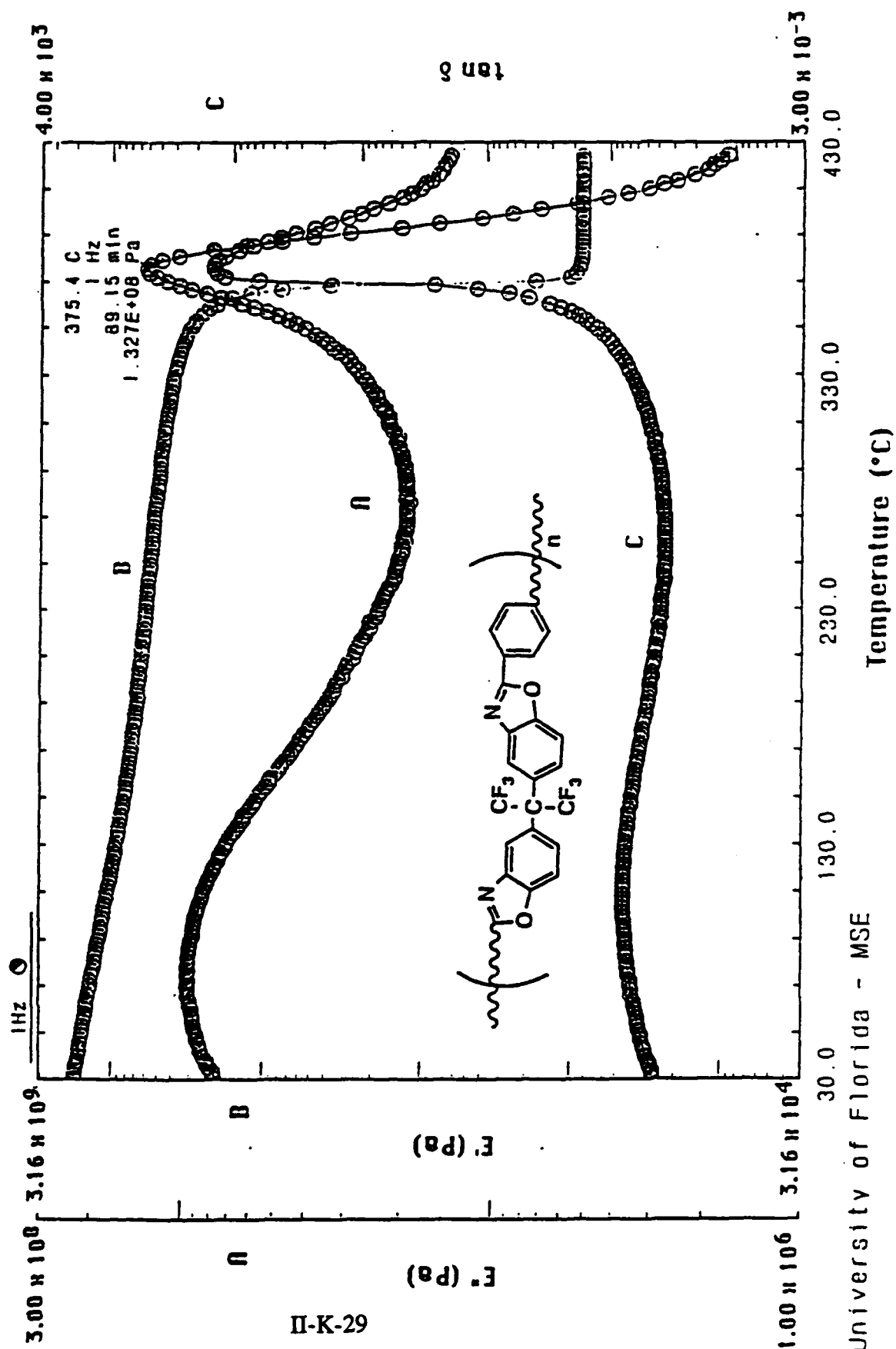
3 Partially cyclized

4 Intrinsic done in NMP at 25°C

5 Tm at 380°C

II-K-28

Dynamic Mechanical Spectrum of 6F-bAP-TC PBO



Conclusions

- * Polyhydroxyamides can be converted to polybenzoxazoles via acid catalyzed, azeotropic distillation in high yields at temperatures as low as 170°C in less than 4 hours. Confirmation of conversion is possible by ¹H NMR, IR and TGA-MS.
- * Acid catalysis by pyridine-hydrochloride is responsible for the accelerated rate of ring closure at lower temperatures.
- * Incorporation of fluorine into the PBO backbone increases the solubility of the polymer as well as promoting solubility during cyclization
- * 6F-bAP-TC PBO's undergo solvent induced crystallization and the extent of crystallization can be altered by exposure time to chloroform.

CONCLUSIONS

- Fully imidized, soluble "3F" polyimides of controlled molecular weight were synthesized from solution imidization techniques.
- Films of PMDA-3F diamine polyimides revealed high T_g's, >420°C, and long term thermooxidative stability. — need further verification
- Processability of the PMDA-3F diamine polyimides is possible by several different routes.
- Fabrication into aircraft engine bushings has been achieved and testing is in progress at GE Aircraft Engines and GE CRD. ^{Current status}
- Major process improvements in 3F diamine have been achieved.
- Semi-crystalline polyimides with T_m 440°C have been prepared.

II-K-31

Went to per
for the
pre- (1987)
affinity

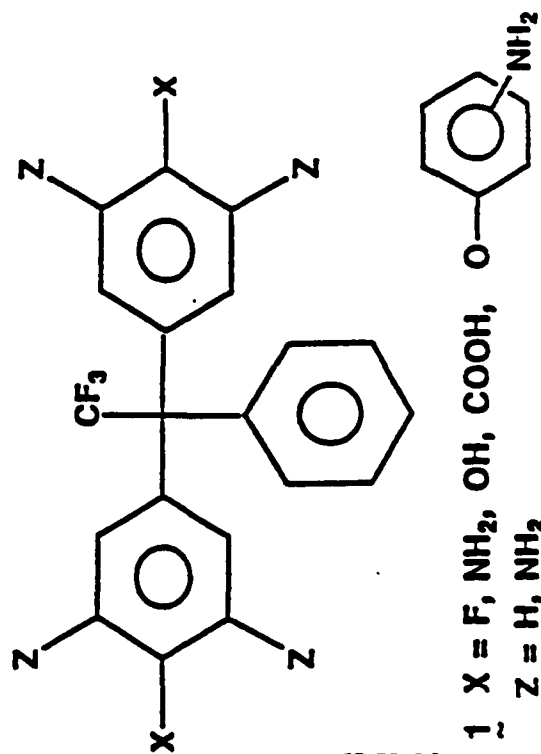
Good copy of 1987 report

FUTURE WORK

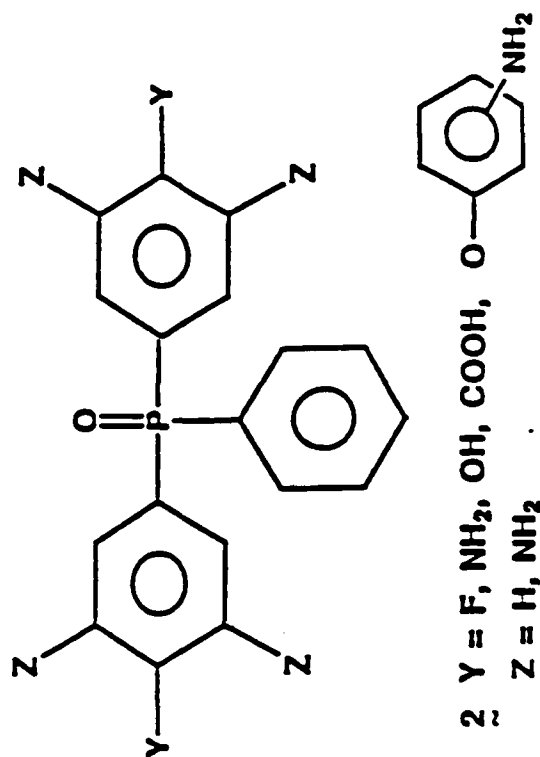
- Continued evaluation of "3F" polyimides for 700°F applications, with emphasis on processing and testing methodologies. *cont. in l.*
- Enhance properties of the "3F" polyimides by incorporation of various comonomers.
- Develop new soluble, high T_g polyimides through the use of phosphorous containing monomers.

phosphorus oxide

High Performance Monomers



II-K-33



- Pendant phenyl groups contribute to soluble, but rigid and thermally stable behavior
- Fluorinated and phosphine oxide structures afford attractive properties

PHOSPHORUS CONTAINING POLYMERS

ADVANTAGES :

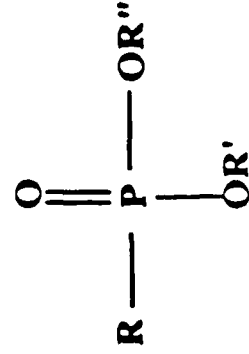
1. UNIVERSALLY IMPARTS FIRE RESISTANCE TO MACROMOLECULAR SYSTEMS
2. REPORTED IMPROVED ADHESION
3. NONVOLATILE OXIDE FORMATION GIVES GOOD OXIDATIVE STABILITY
4. POSSIBILITY OF FURTHER CHEMISTRY ON POLYMERS

p=0 complete by itself

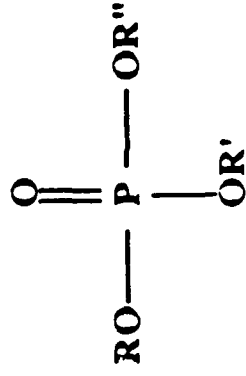
DISADVANTAGES:

1. ONLY LOW MOLECULAR WEIGHT OLIGOMERS HAVE BEEN REPORTED
2. MONOMERS DIFFICULT TO PREPARE/PURIFY
3. PHOSPHORUS PRESENCE INTERFERES WITH MANY CATALYSTS
4. PHOSPHORUS-OXYGEN BONDS ALONG POLYMER CHAINS HYDROLYTICALLY UNSTABLE

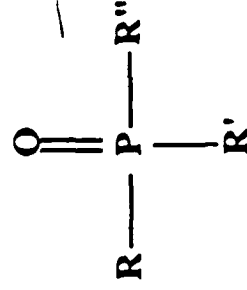
TYPICAL FORMS OF PHOSPHORUS INCORPORATED INTO POLYMERS:



PHOSPHONATE



PHOSPHATE



PHOSPHINE OXIDE

highly reactive, stable

ENGINEERING OBJECTIVES

- Develop methodology for preparation of dispersed, submicron, high performance thermoplastics and reactive thermosets.
- Develop prepregging and consolidation methods for fiber-reinforced polymer, polymer/metal, and polymer/ceramic composites. *Can do. sub microns per fiber*
- Develop test methods for evaluating mechanical, electrical, and thermal properties of novel composites. *blend ceramic w/ polymer*

LINEAR AND NETWORK MATERIALS

THERMOSETS

Large Data Base
Low Initial Viscosity
"Chemistry" During Processing
Finite Shelf Life
Excellent Chemical Resistance
Often Brittle

THERMOPLASTICS

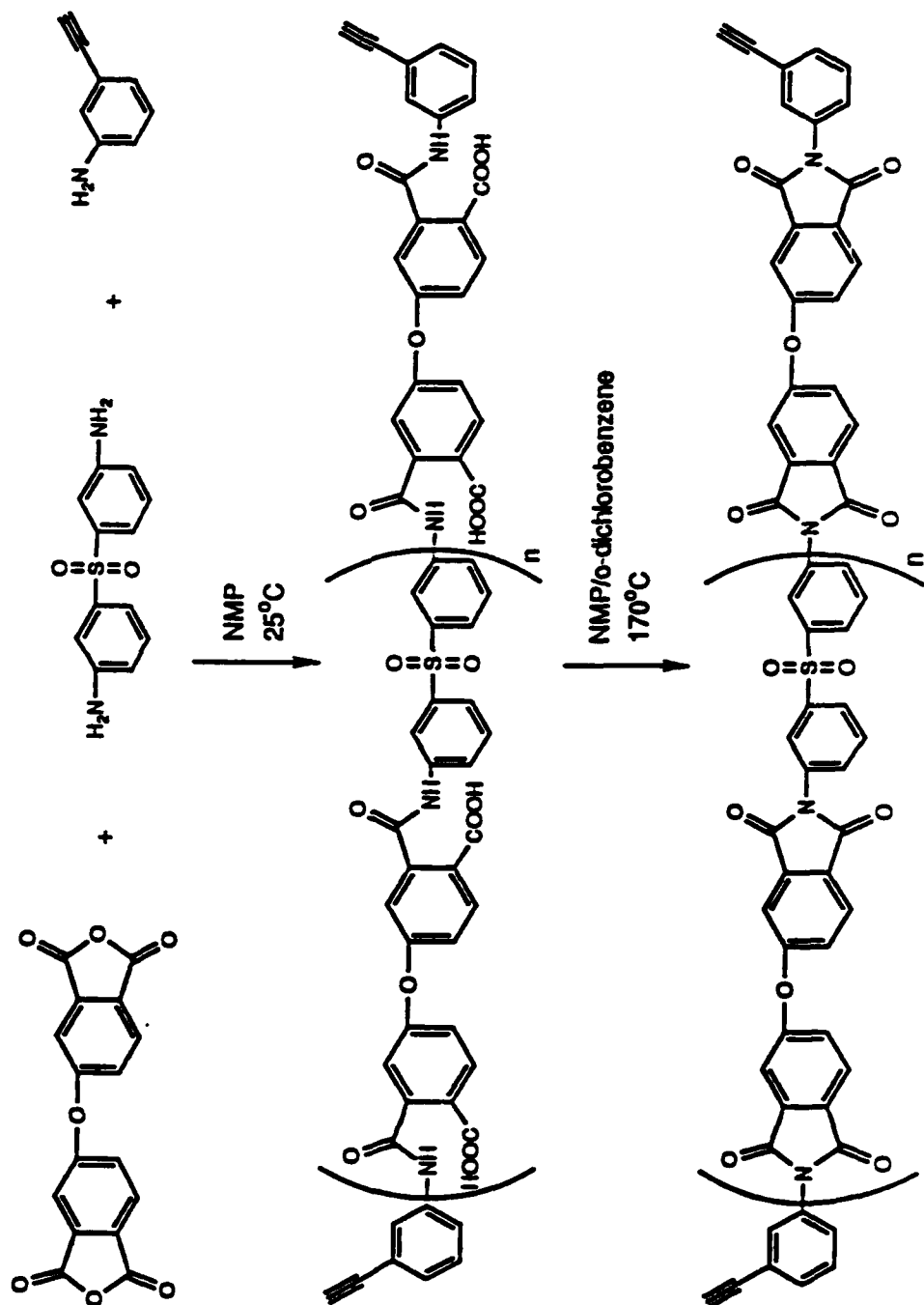
Small Data Base
High Viscosity
Minimal "Chemistry" During Processing
Storage Possible
Morphology Determines Chemical Resistance
Usually Ductile

GENERAL NEEDS

- Tougher Thermosets
- Improve Processibility of Thermoplastics

Synthesis Of Acetylene Functionalized

ODPA/3,3'DDS Polyimide



ACKNOWLEDGEMENTS

**THE INVESTIGATORS LIKE TO ACKNOWLEDGE
THE SUPPORT OF THIS PROJECT BY:**

(a) Fundamental Monomer Studies

**NATIONAL SCIENCE FOUNDATION SCIENCE AND TECHNOLOGY
CENTER FOR HIGH PERFORMANCE ADHESIVES AND COMPOSITES**

(b) Major Activities Since May 1, 1991

DARPA/ARO

VIRGINIA TECH

CLEMSON UNIVERSITY

Professor Mark C. Thies

**SUPERCritical FLUID EXTRACTION:
A NEW PROCESS FOR PRODUCING
HIGH-PERFORMANCE CARBON FIBERS**

DAAL03-89-K-0067

**Department of Chemical Engineering
Center for Advanced Engineering Fibers
Clemson University, Clemson SC**

**M. C. Thies
D. D. Edie
J. C. Mullins
G. C. Lickfield
G.-Z. Liu
K. E. Robinson**

**K. W. Hutchenson
J. R. Roebers
T. Hochgeschurtz
G. Bolanos
J. W. Chastain
S. B. Wilde
J. K. Davis**

SUPERCRITICAL FLUID EXTRACTION: A NEW PROCESS FOR PRODUCING HIGH-PERFORMANCE CARBON FIBERS

- **Introduction**
- **Experimental Apparatus**
- **Results**
 - **Phase Equilibria**
 - **Pitch Characterization**
 - **Fiber Spinning**
 - **Fiber Characterization**
- **Conclusions**

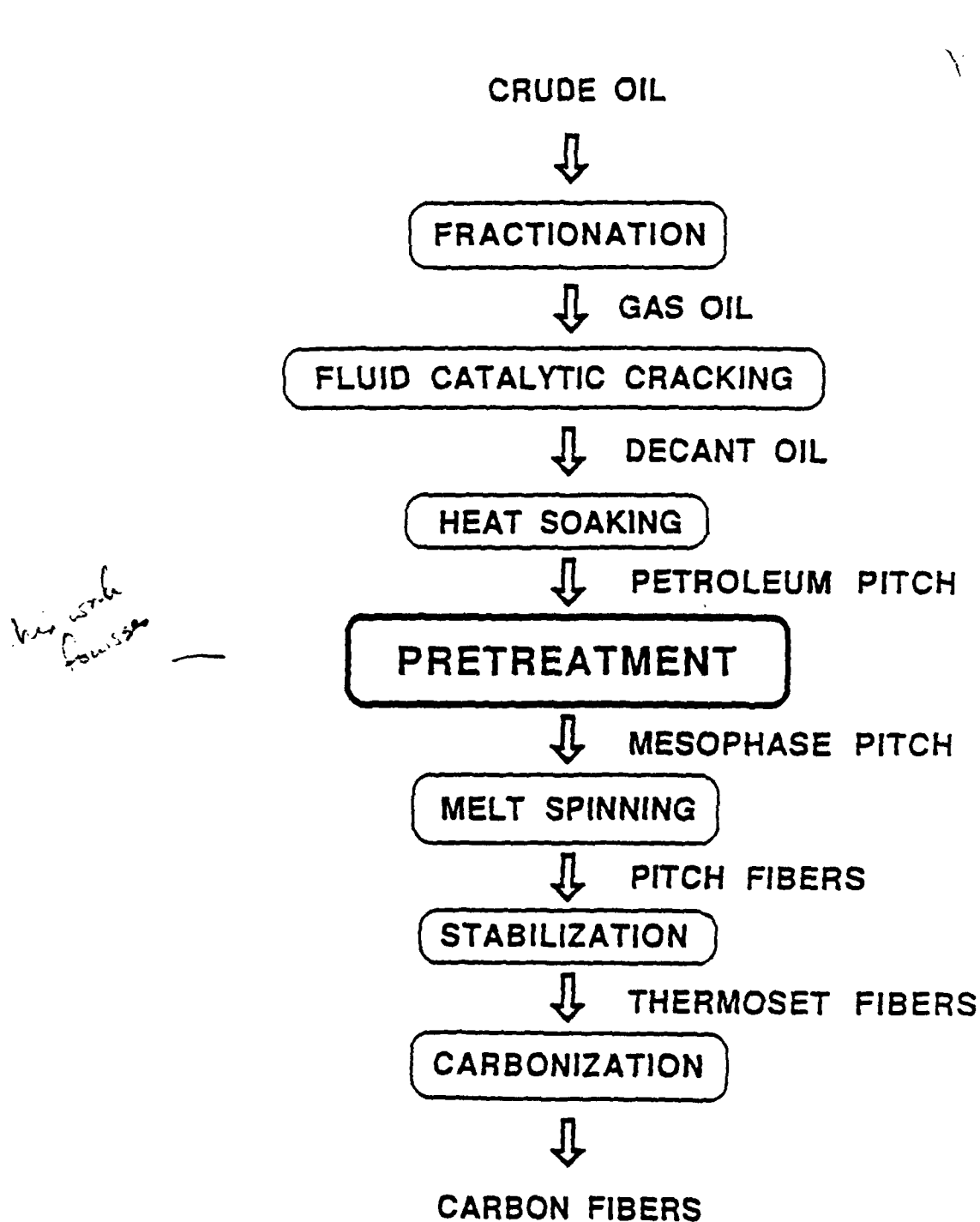
INTRODUCTION

- Mesophase Pitch Potentially Can be Used to Produce Lower-Cost, High-Performance Carbon Fibers
- Composition of Mesophase Pitch Affects Properties of Resultant Carbon Fibers
- Our Objective is to Develop a SCF Extraction Process for Producing a Superior Mesophase Pitch

Anticipated Accomplishments

- **Produce a Superior Precursor Pitch for Spinning Carbon Fibers**
- **Manufacture Economical High-Performance Carbon Fibers**

PRODUCTION OF PITCH-BASED CARBON FIBERS

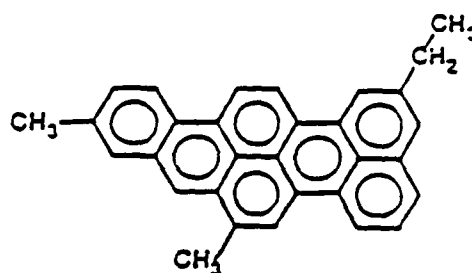


ASHLAND A-240 PETROLEUM PITCH

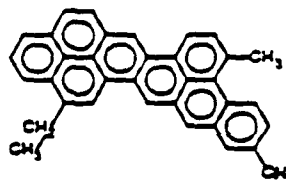
Typical Elemental Composition

91 wt % C
6 wt % H
2 wt % S
0.5 wt % N
0.5 wt % O

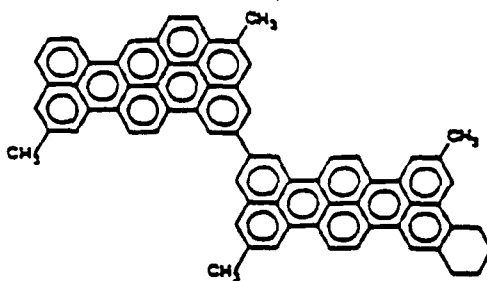
A-240 Pitch, MW 433



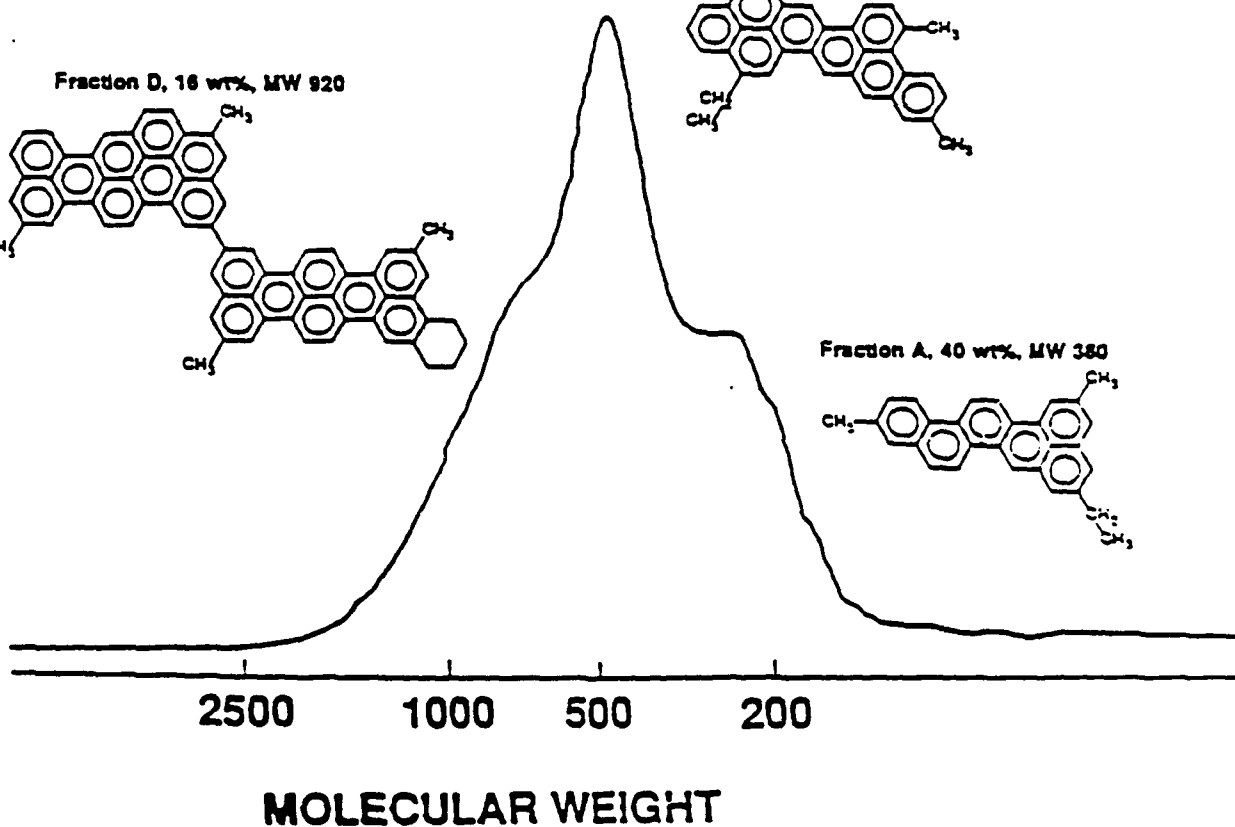
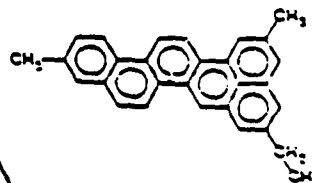
Fraction B, 32 wt%, MW 445



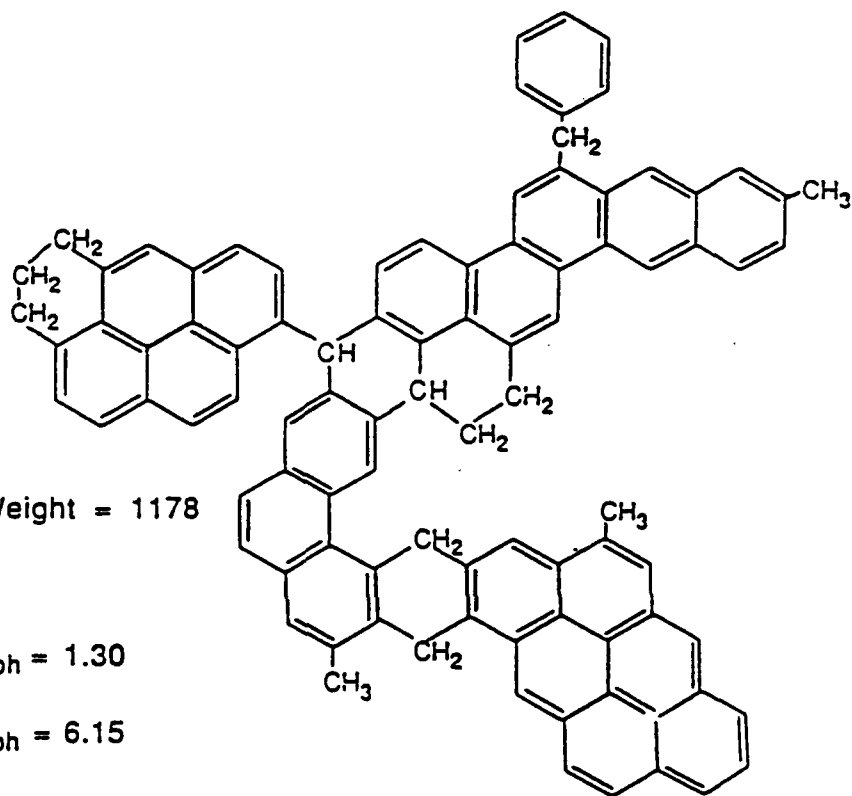
Fraction D, 18 wt%, MW 920



Fraction A, 40 wt%, MW 380



Structures by E.M. Dickinson, *FUEL*, 64, 704 (1985)



Molecular Weight = 1178

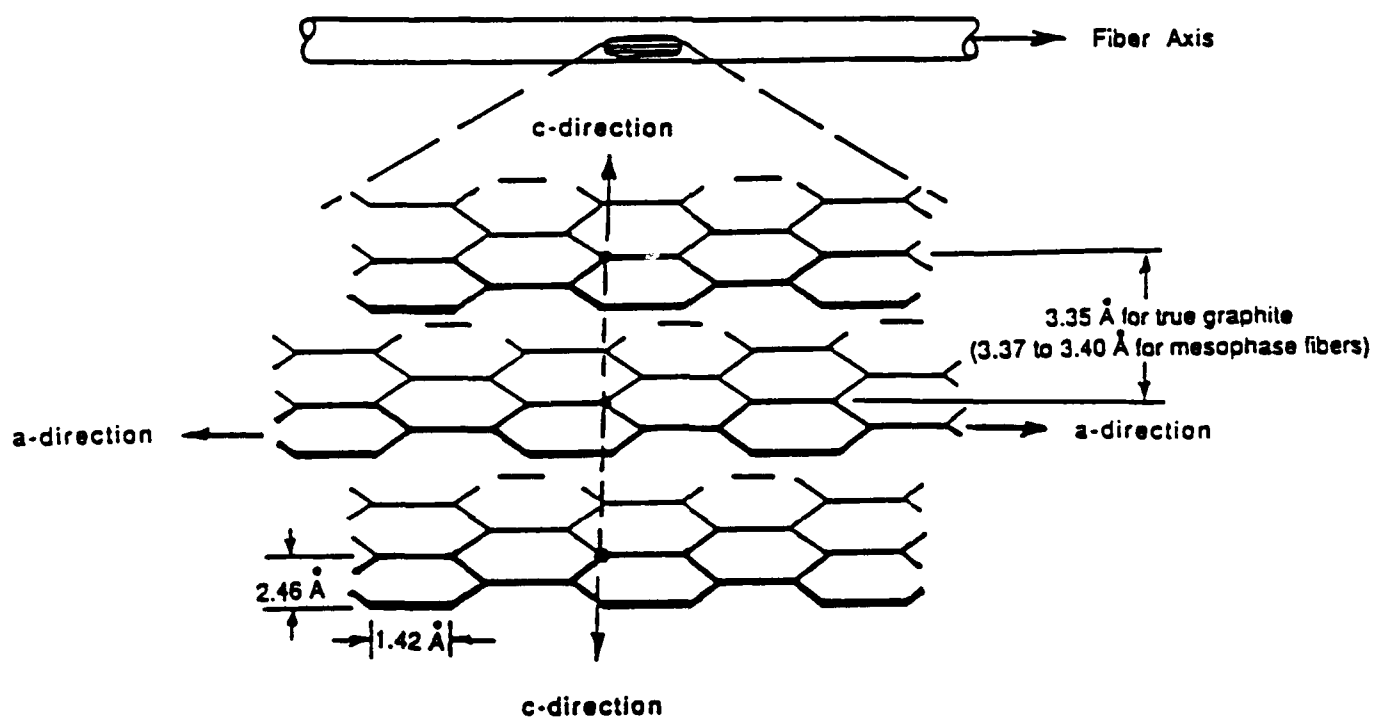
C / H = 1.50

H_{arom} / H_{aliph} = 1.30

C_{arom} / C_{aliph} = 6.15

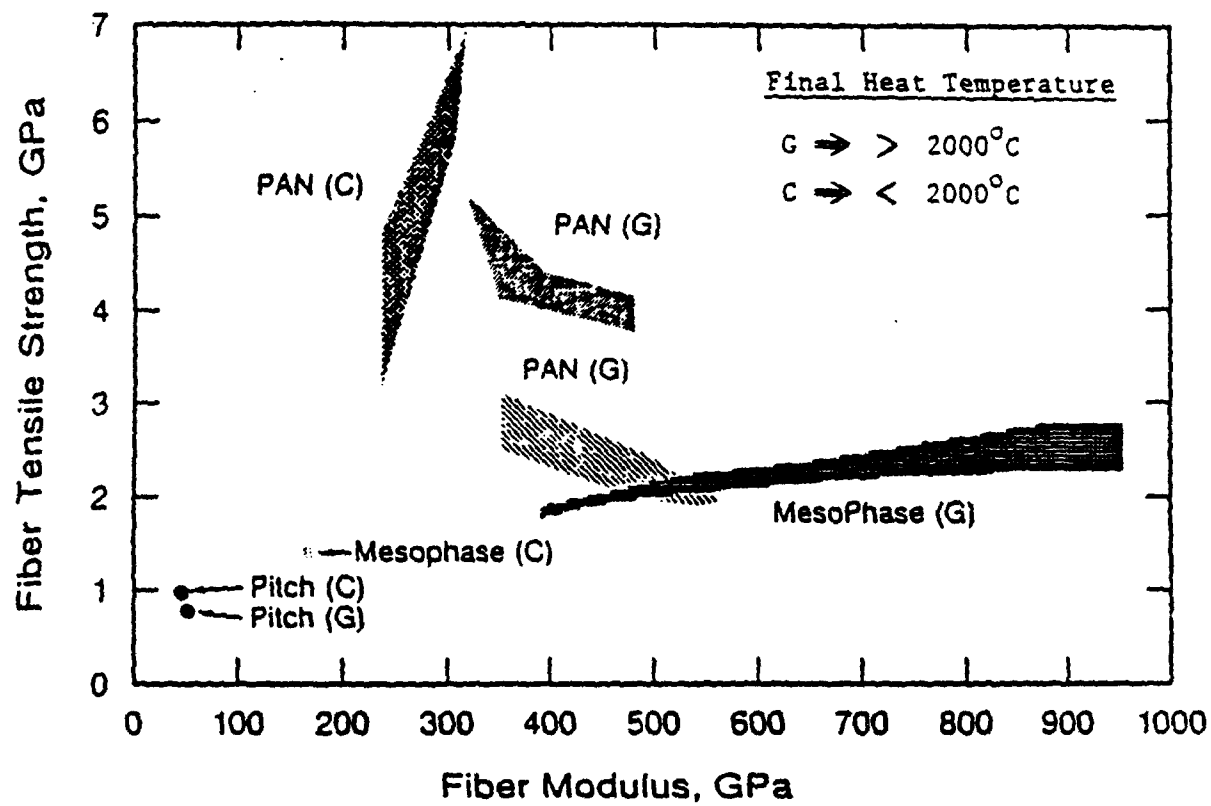
A Typical Molecule in Mesophase Pitch

*Want
MW ~ 1000*

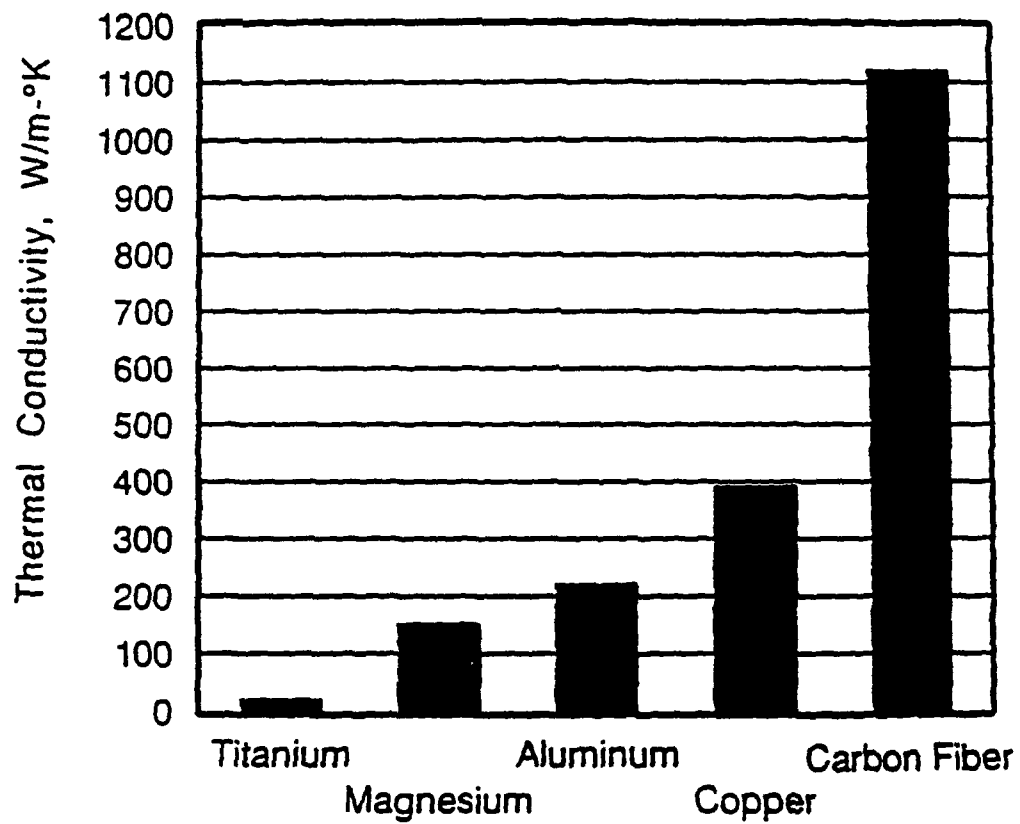


Structure of Pitch-Based Carbon Fibers

TENSILE STRENGTH AND MODULUS OF VARIOUS TYPES OF CARBON FIBERS



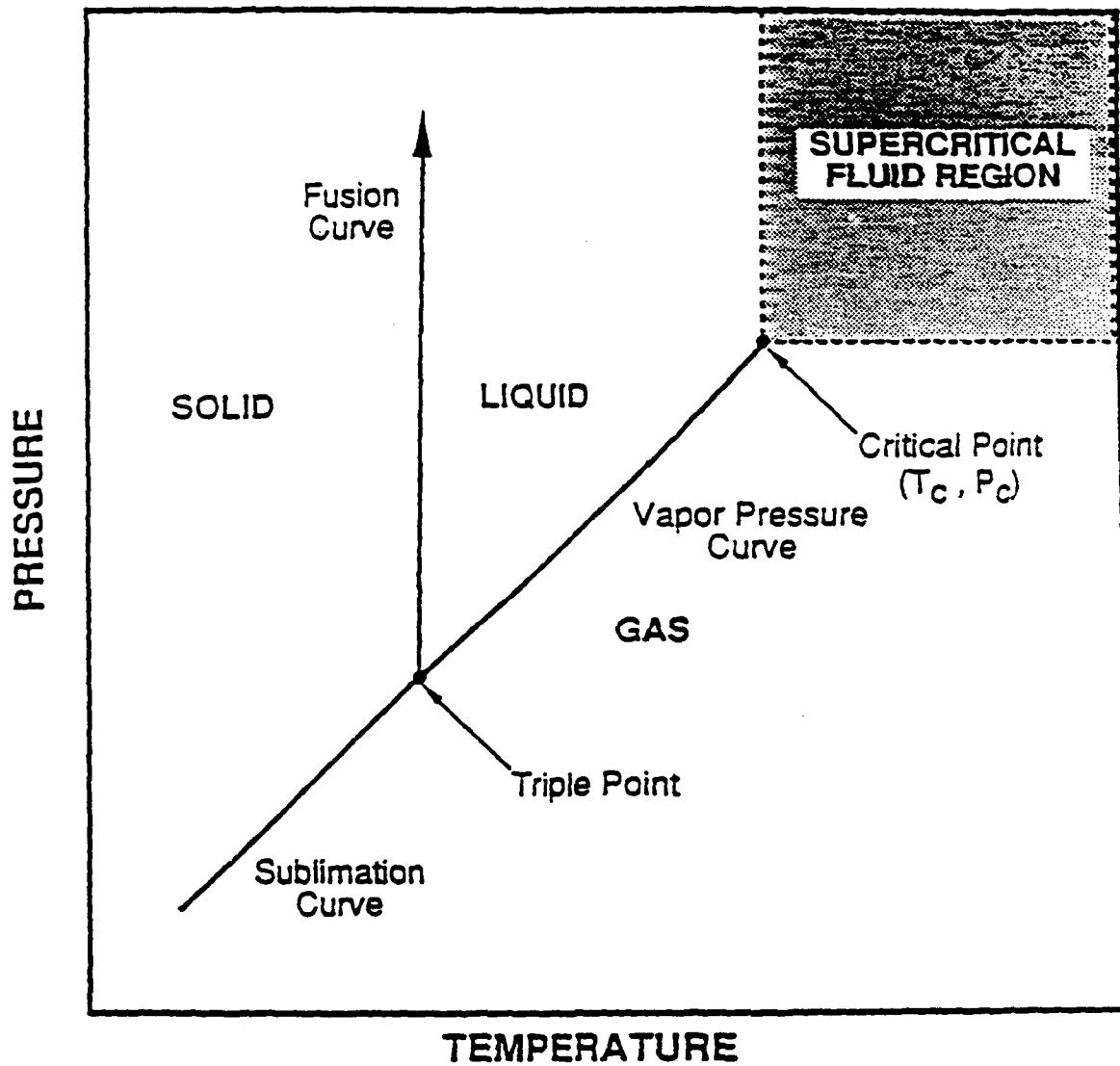
*pitch stiff
but not strong*



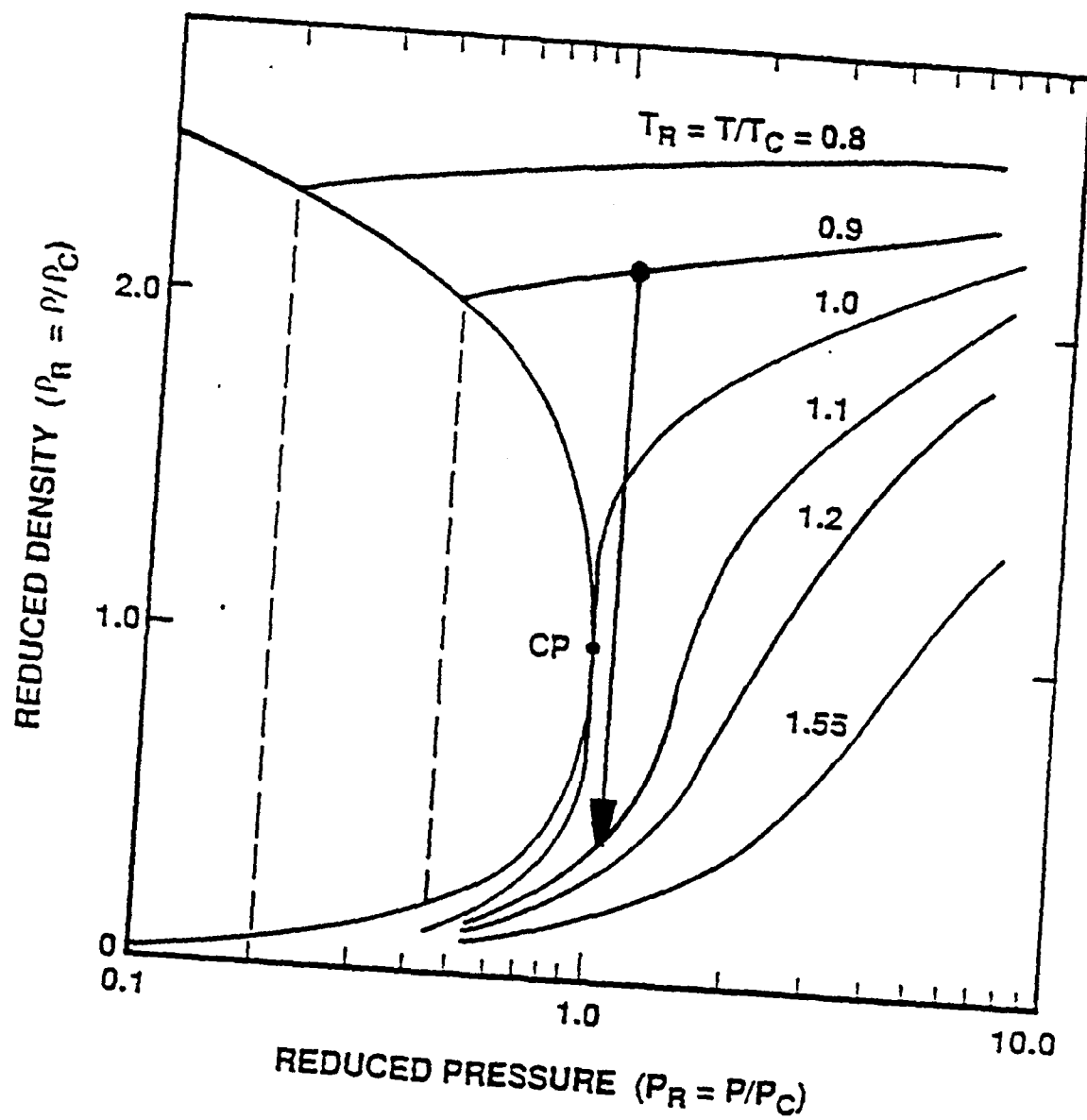
Thermal Conductivity of Various Materials

*3x that of
Copper*

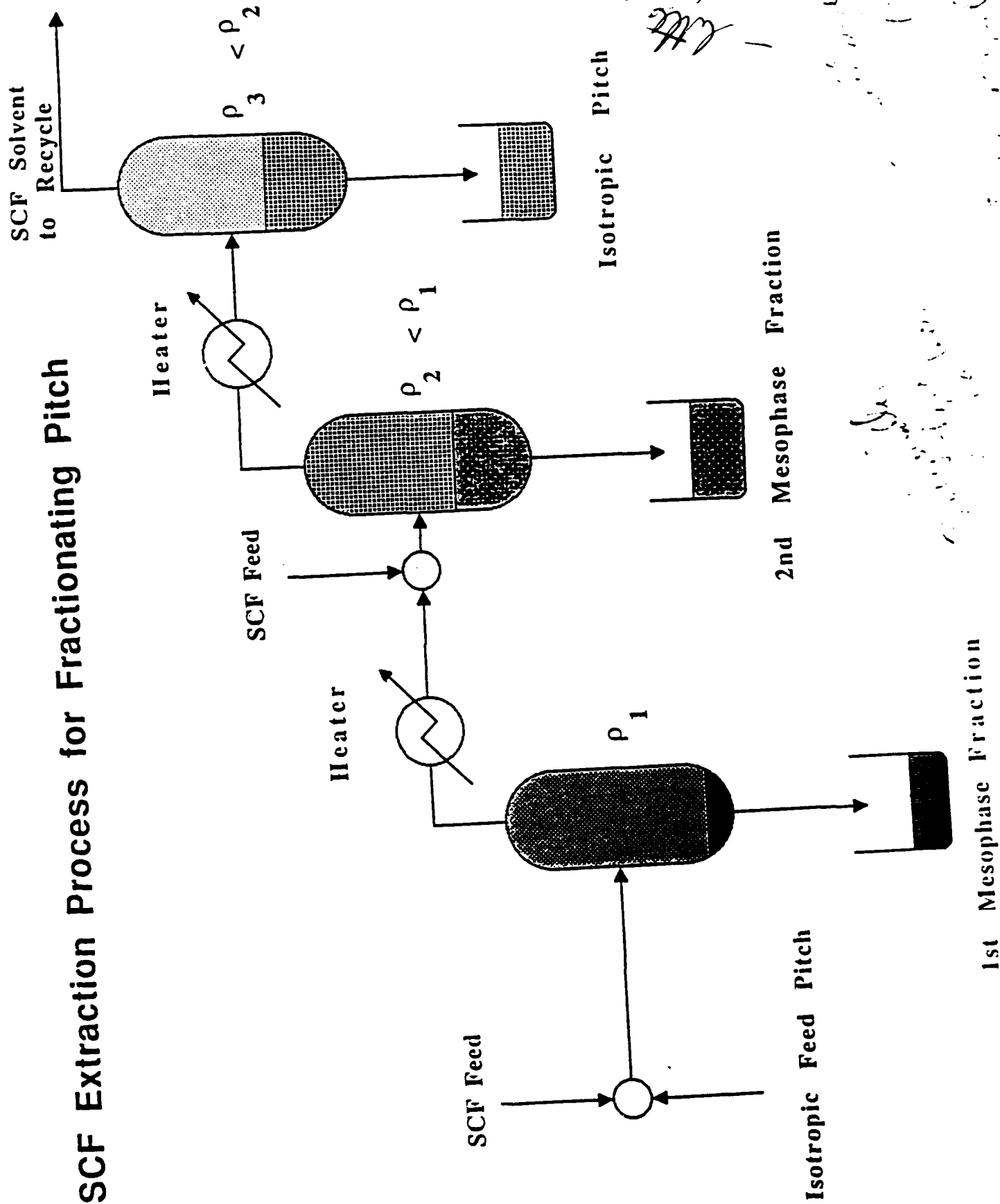
Pressure-Temperature Diagram for a Pure Fluid



$\rho_R - P_R$ Diagram for a Pure Fluid



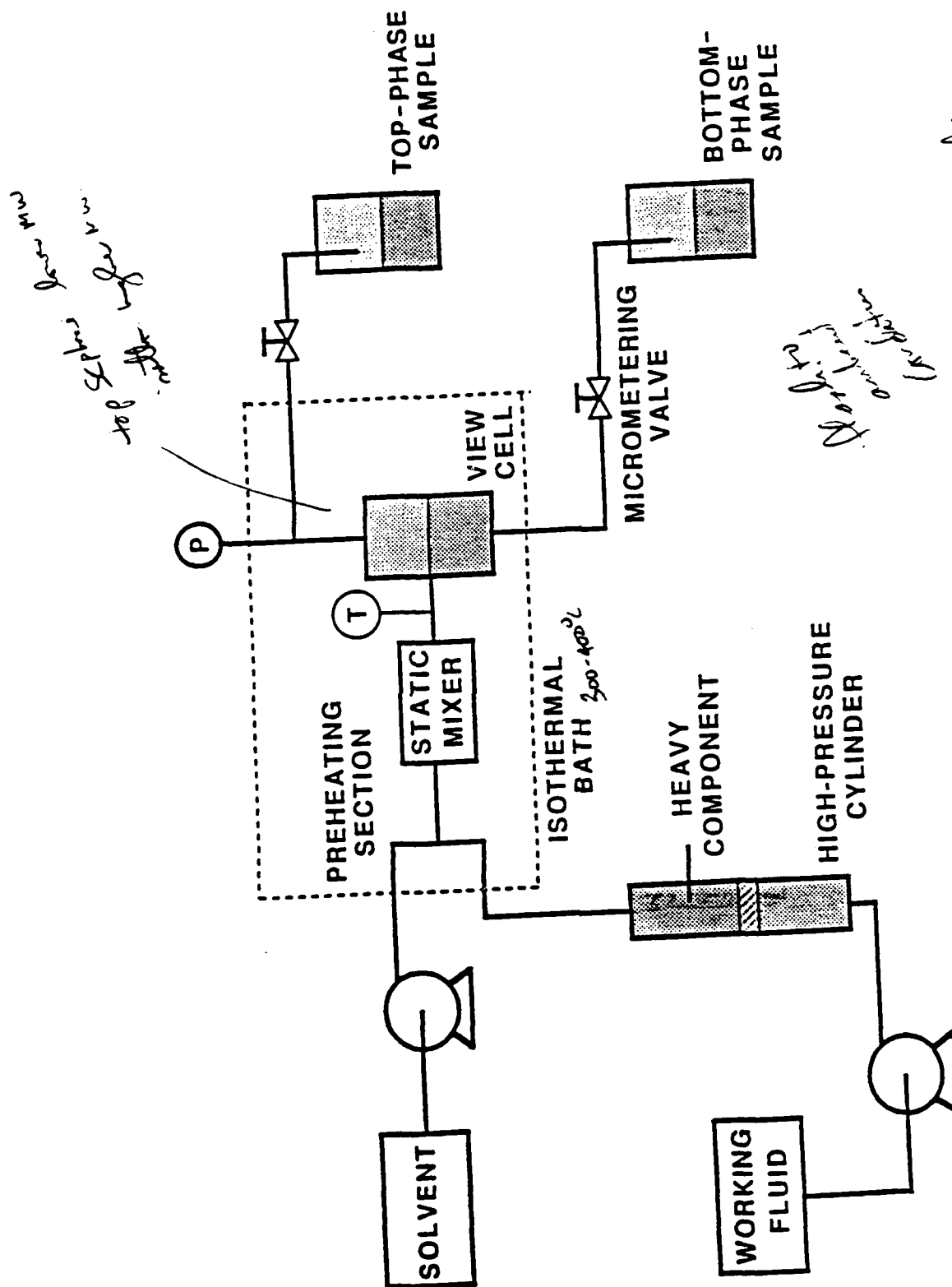
SCF Extraction Process for Fractionating Pitch



Potential Advantages of SCF Extraction Process

- Ability to Control Molecular Weight Distribution of Mesophase Pitch
- Additional Technique for Removing Solid Impurities
- Continuous Operation is Significant Advantage for Industrial Production

*every process now used is
batch*

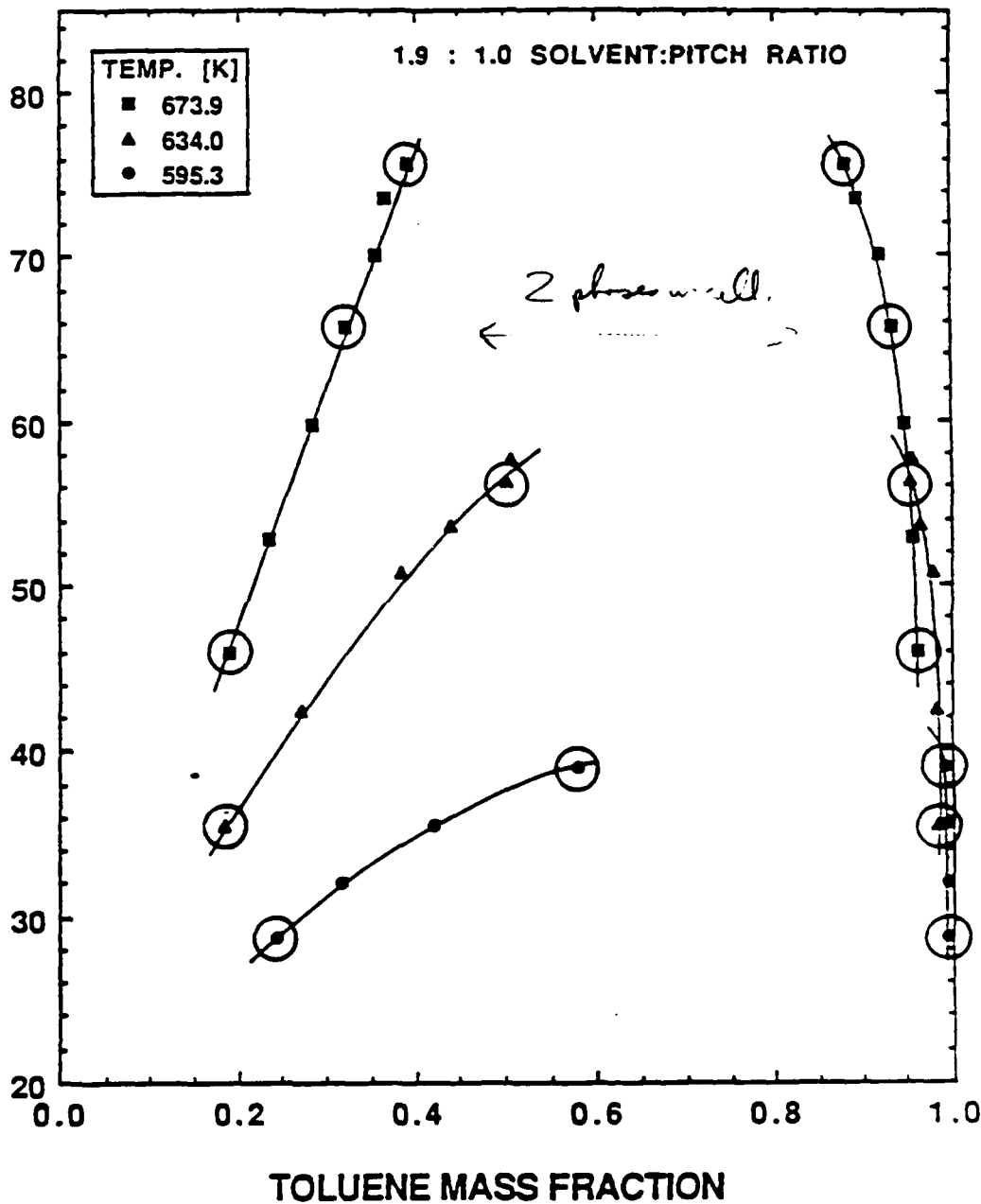


Pitch Extraction Apparatus

*Vapor
liquid
region*

PHASE DIAGRAM ASHLAND A-240 PITCH / TOLUENE

*Common
region
of
stable
CF content
not well
defined
they
looked
at it
it was
no phase*



*Not able to find mesophase at any of these
conditions*

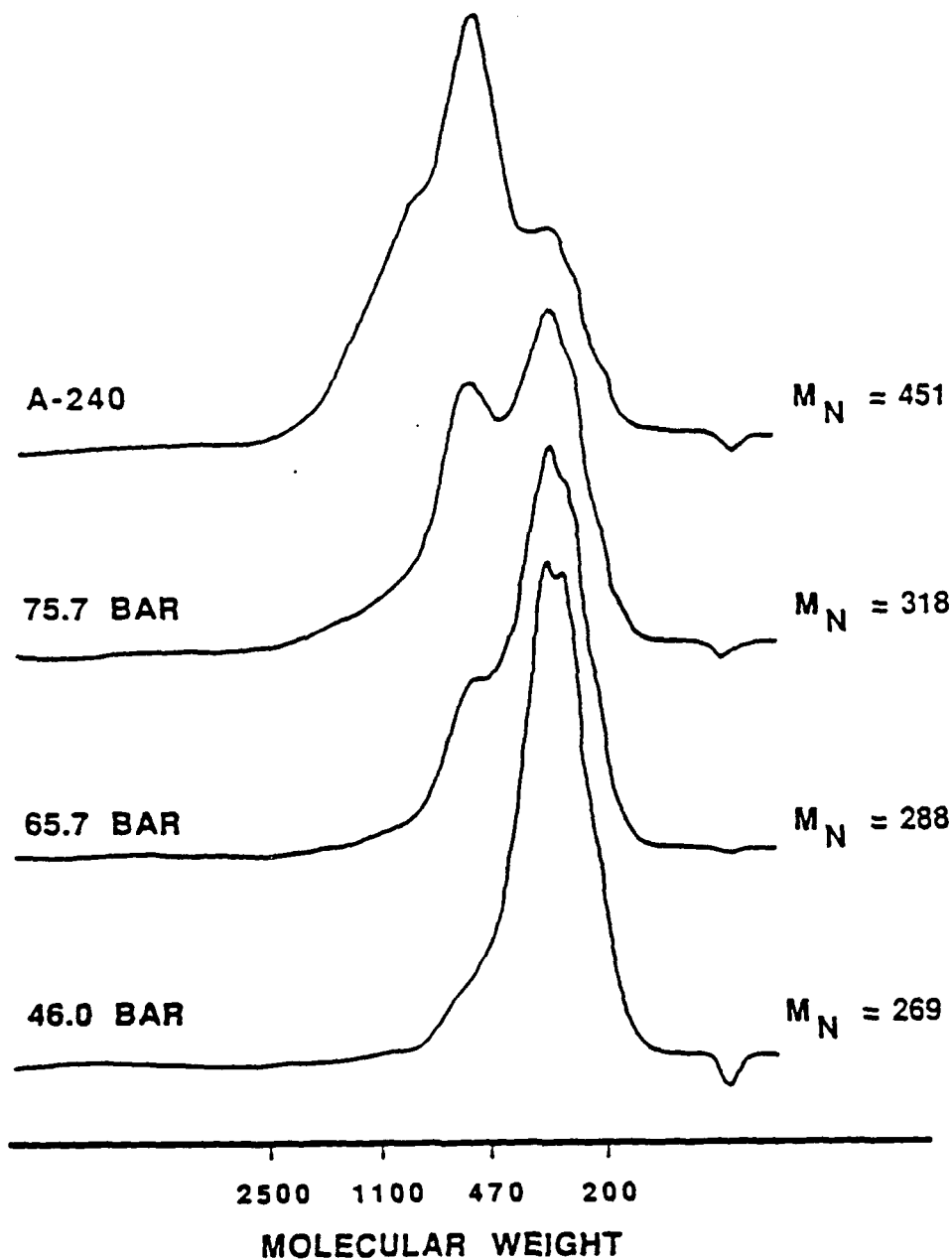
MWD OF A-240 AND TOP PHASE FRACTIONS

SCF-EXTRACTION

TEMPERATURE: 673.9 K
TOLUENE / PITCH RATIO: 1.9 / 1.0

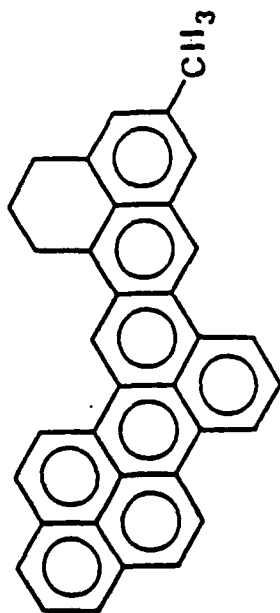
GEL-PERMEATION CHROMATOGRAPHY

ELUENT: TCB @ 1ml/min, 80 °C
COLUMNS: 500 Å / 100 Å PLgel 10 μ m
DETECTOR: REFRACTIVE INDEX

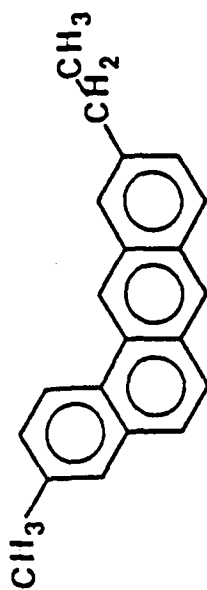


AVERAGE MOLECULAR STRUCTURES A-240 AND TOP PHASE FRACTIONS (673.9 K)

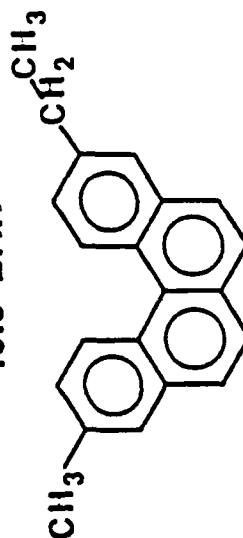
A-240 PITCH



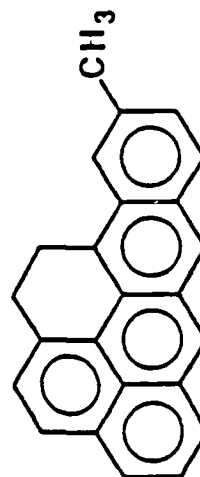
65.7 BAR



46.0 BAR

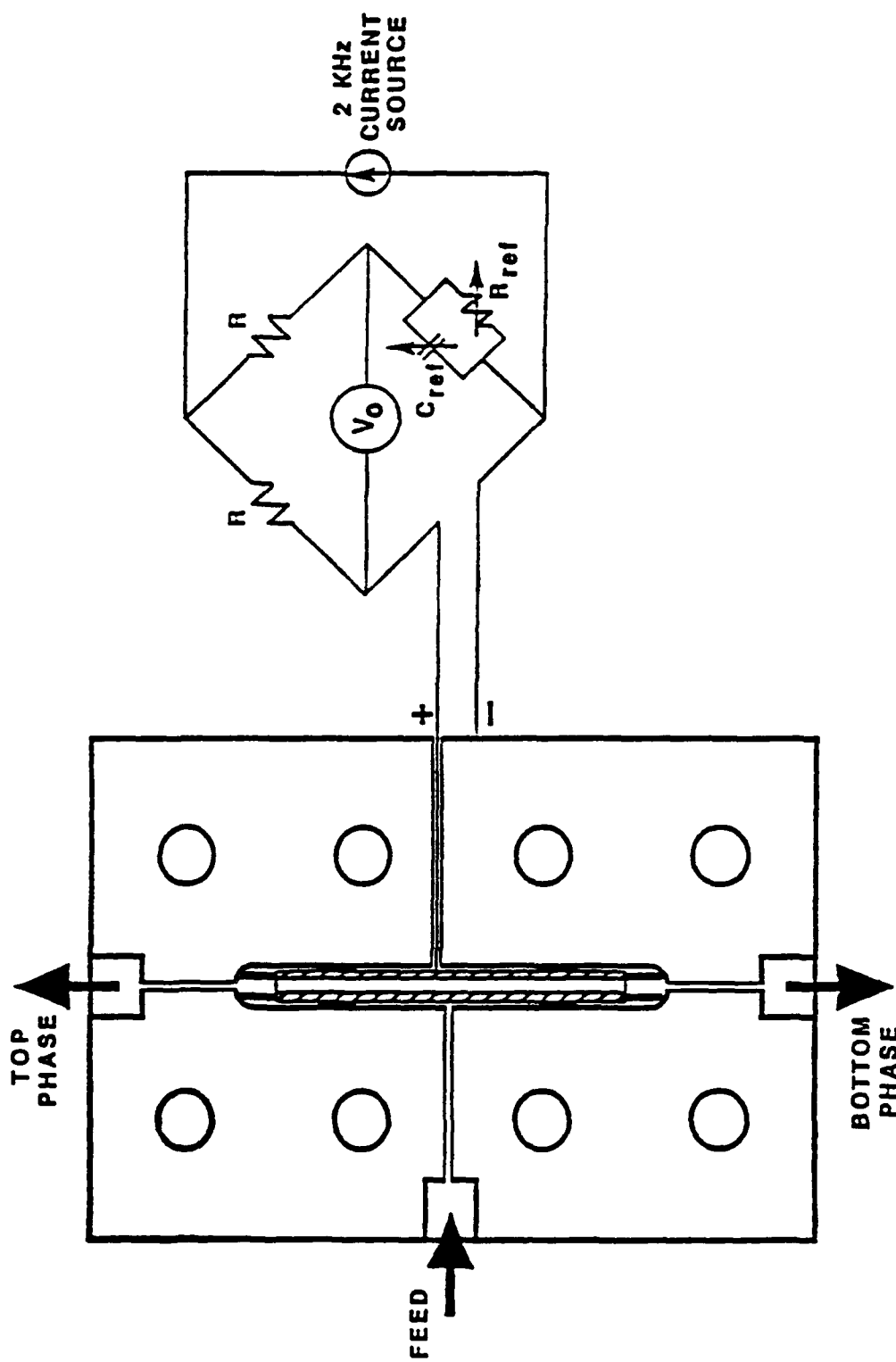


75.7 BAR



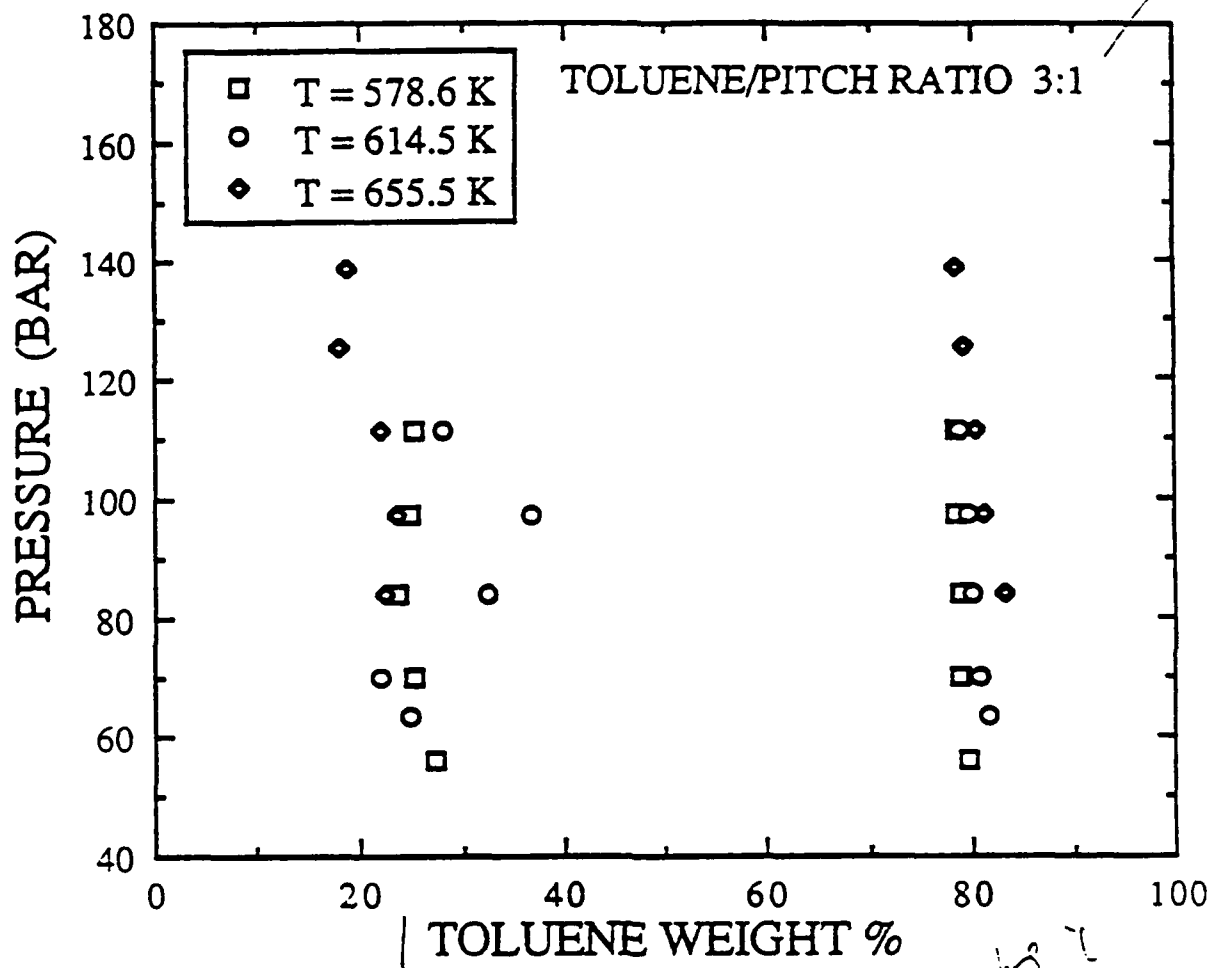
FRACTIONATION OF A-240 PITCH WITH SCF TOLUENE

- Extracted pitch fractions demonstrate that SCF toluene is effective in separating pitch fractions by MW
- due to this, it did not* • In vapor-liquid region, extract yields are too low for the unextracted phase to spontaneously produce mesophase pitch *needed higher pressure*
- A liquid-liquid region was discovered in which significant amounts of pitch were extracted, but both phases were opaque
- A nonvisual technique had to be developed for interface detection

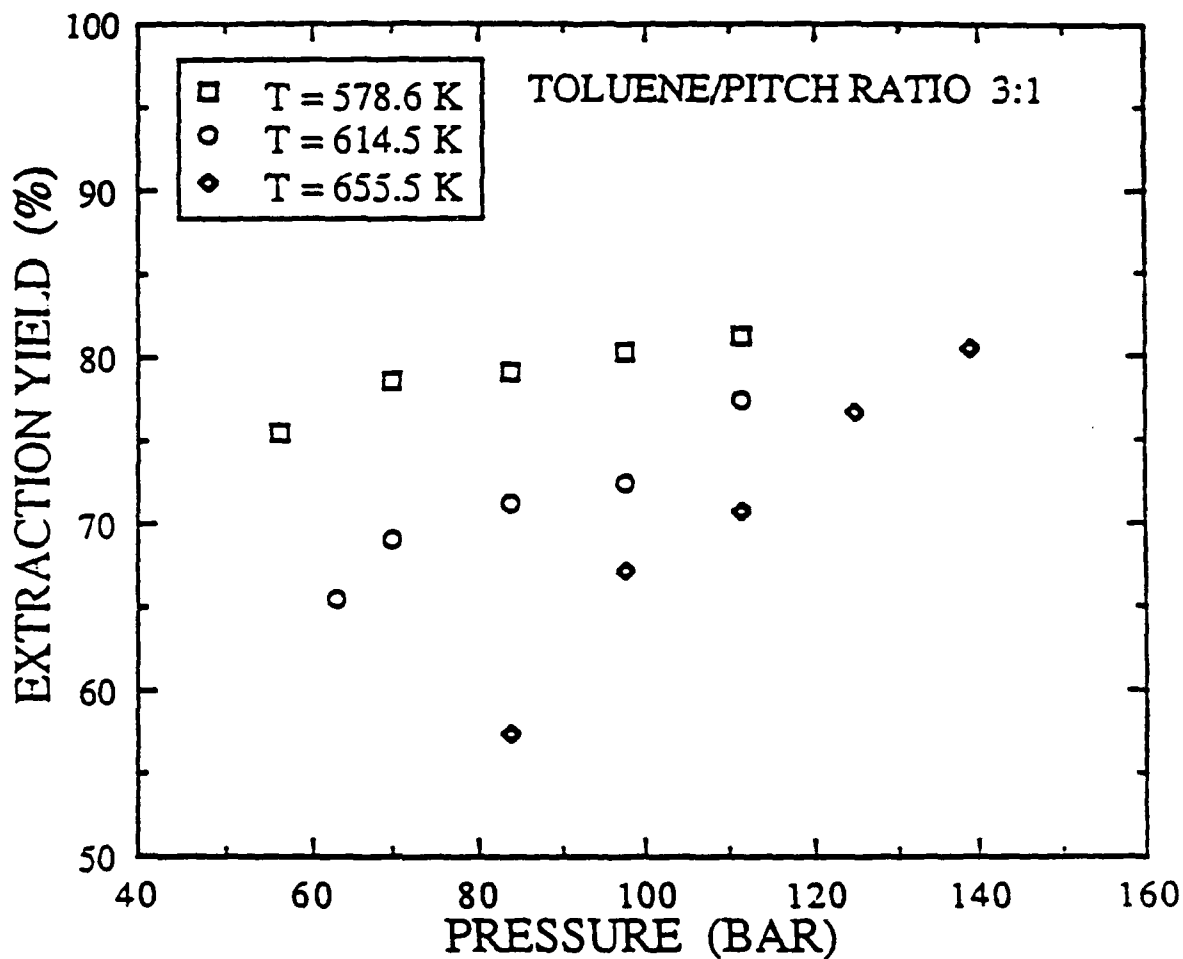


II-L-22

View Cell, Internal Electrode, and Impedance Bridge



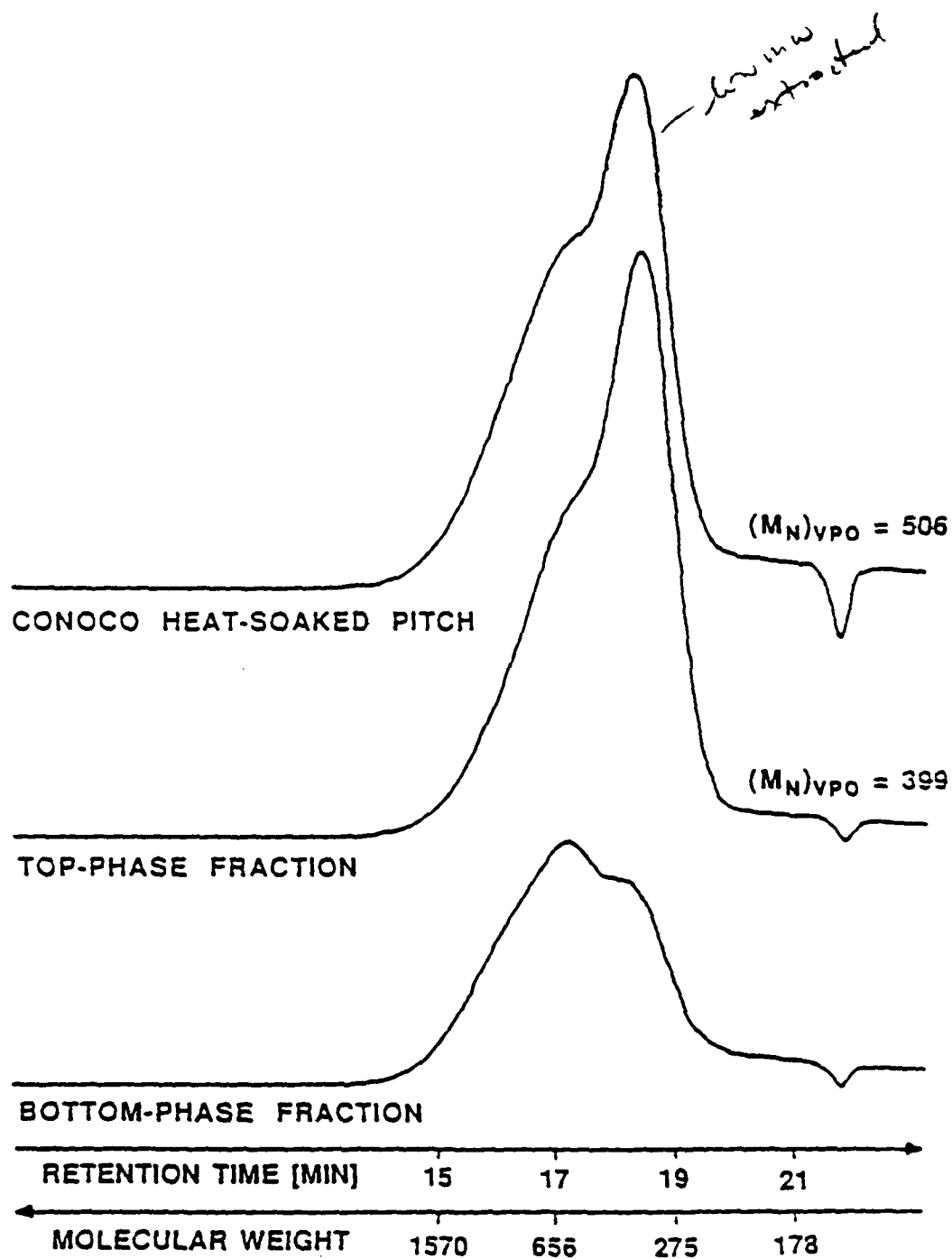
**LLE for Toluene/Pitch System at
578.6, 614.5, and 655.5 K**



**Extraction Yields for Toluene/Pitch System at
578.6, 614.5, and 655.5 K**

II-L-24

*As charge P
yield increases
extracting low MW into soft
decreasing mass on
balance*



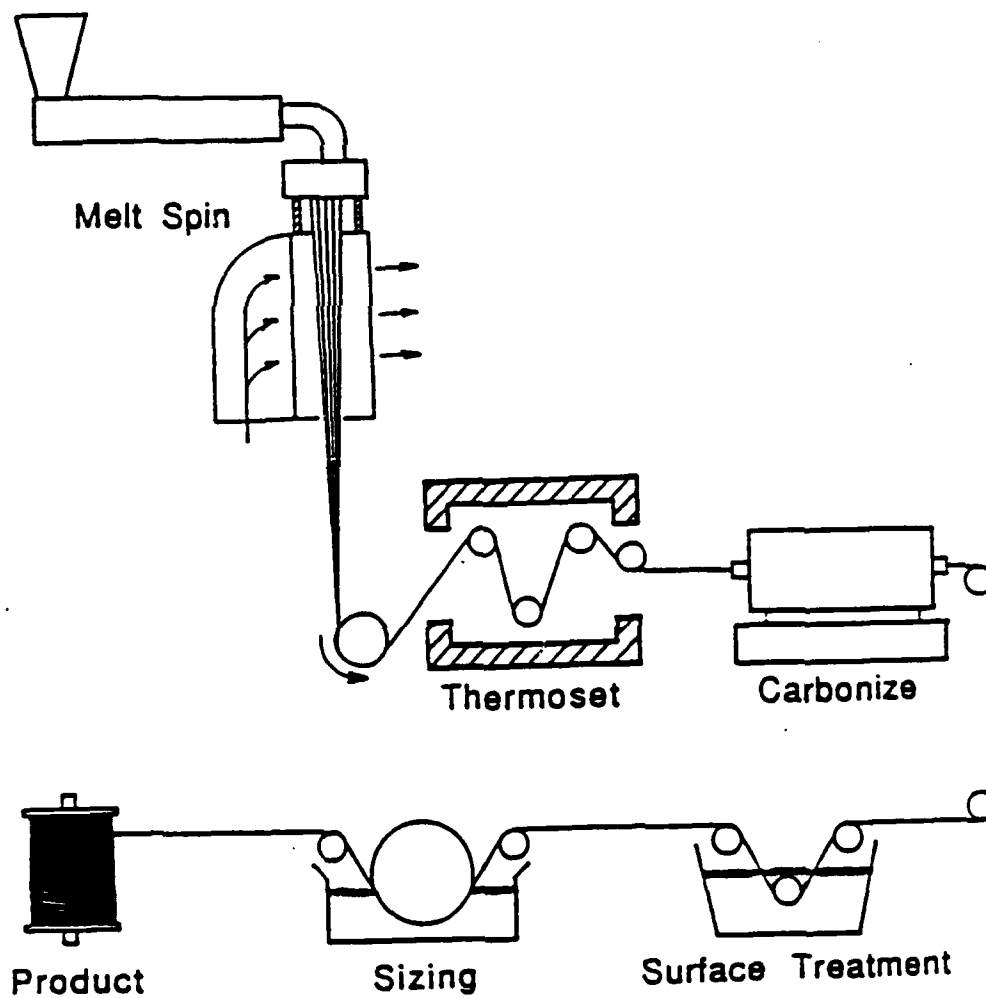
MWD of Feed Pitch, Top-Phase, and Bottom-Phase Fractions (614.5 K, 70 bar)

II-L-25

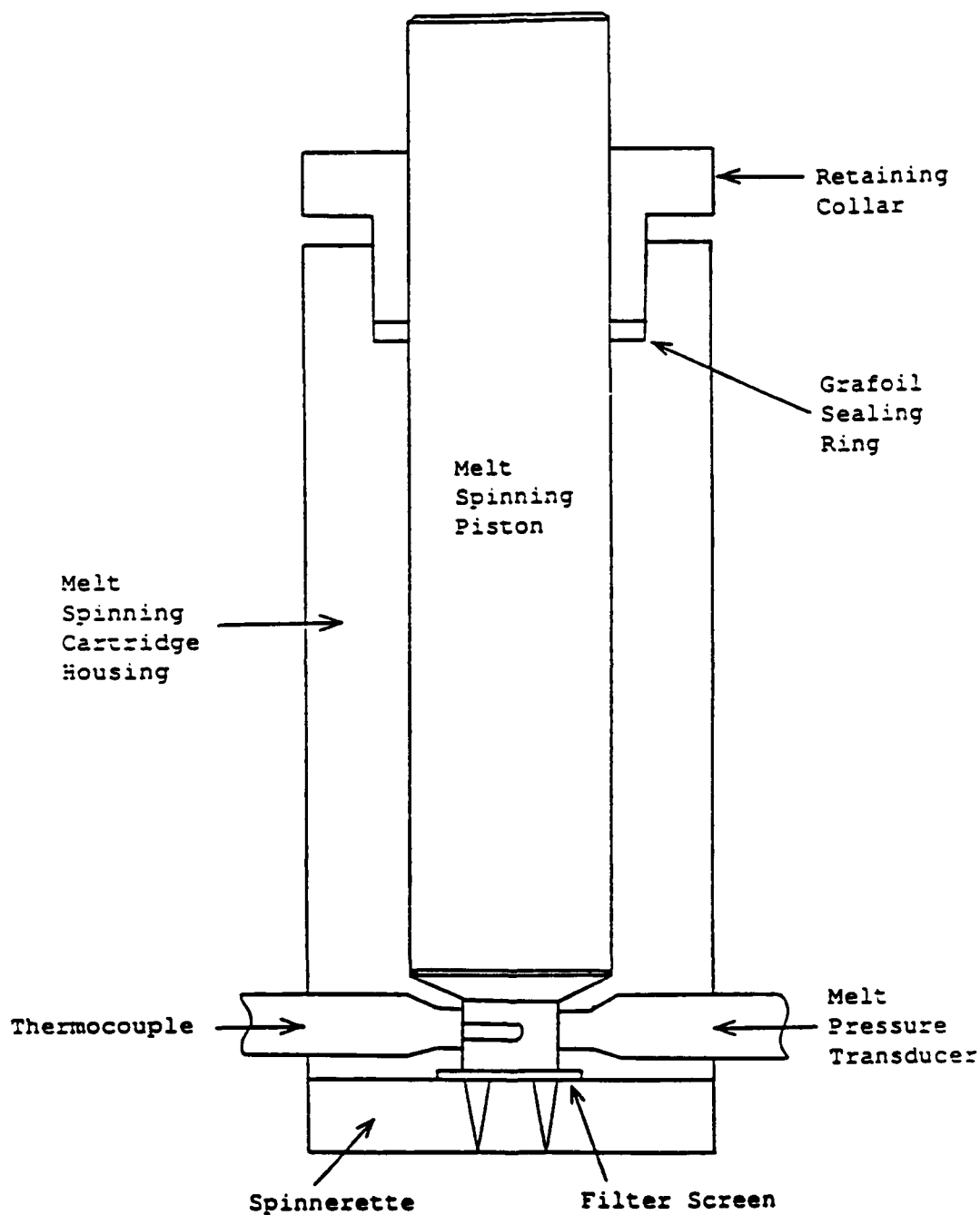
Properties of Mesophase Selected for Spinning

1-nd sample 320-340 °C

- Extracted with SC Toluene at 340 °C and 70 bar and Solvent-to-Feed Ratio of 3:1
- Vacuum-Dried Rapidly Under Nitrogen at 360 °C to Remove Excess Toluene*
- 100% Mesophase by Polarized Light Microscopy*
- Softening Point of 305 °C
- Viscosity-Temperature Relationship Determined with Capillary Rheometer



Schematic of Pitch-Based Carbon Fiber Process



Batch Melt-Spinning Apparatus

II-L-28

P. 61

Spinning Conditions for Mesophase Produced by SCF Extraction

Property or Variable

Spinning Temperature (°C)	360
---------------------------	-----

Pressure (bar)	40
----------------	----

Mass Flow Rate (g/s)	0.04
----------------------	------

Winder speed (m/s)	<i>easy to spin</i> 9.8
--------------------	-------------------------

Quench Air Temperature (°C)	27
-----------------------------	----

Spinnerette	12 hole, 200 μm
-------------	----------------------------

Filter Type	18 μm screen
-------------	-------------------------

Heat Treatment Conditions of Fibers Melt-Spun From Mesophase Produced by SCF Extraction

Stabilization:

Heating rate: 5 °C/min (from 20 to 180°C)
1 °C/min (from 180 to 280°C)
Final temperature: 280 °C
Holding time: 80 or 120 min

Carbonization:

Heating rate: 20 °C/min
Final temperature: 2400 °C
Holding time: 15 min

✓ can produce
better
ygo to higher
C carbonization

Final Mechanical Properties of Fibers Melt-Spun From Mesophase Produced by SCF Extraction*

SCF Conditions	Fiber Diameter (μm)	Tensile Strength (GPa)	Tensile Modulus (GPa)	Elongation to Failure (%)
340 °C, 70 bar	24 \pm 5	0.99 \pm 0.38	360 \pm 120	0.6 \pm 0.2
380 °C, 125 bar	38 \pm 12	0.97 \pm 0.55	550 \pm 480	0.7 \pm 0.3

Gauge Length = 10.0 mm

Number of Filaments Tested = 20

*Pitch was not properly devolatilized

could be 4 or 5?

HF

Final Mechanical Properties of Pitch-Based Carbon Fibers Melt-Spun From Different Mesophases

Mesophase Type	Fiber Diameter (μm)	Tensile Strength (GPa)	Tensile Modulus (GPa)	Elongation to Failure (%)
Heat-soaked	12.1 \pm 0.6	2.2 \pm 0.4	360 \pm 80	0.62 \pm 0.18
Mitsubishi	7.0 \pm 0.3	3.1 \pm 0.8	800 \pm 160	0.48 \pm 0.09
SCF-extracted	9.0 \pm 0.4	3.3 \pm 1.1	820 \pm 230	0.58 \pm 0.16

after strength
from Japan

Gauge Length = 10.0 mm
Number of Filaments Tested = 30-40

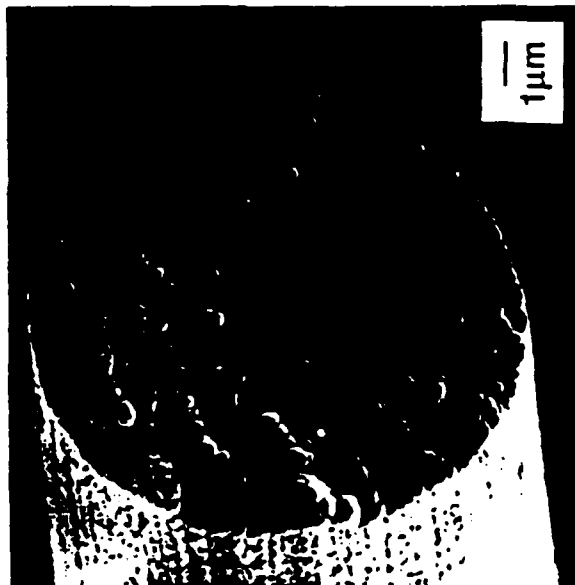
II-L-32

Amoco

did not
test fibers
from Japan

used for strength

SEM Micrographs of Round-Shape Fibers



Heat-Soaked



SCF-Extracted



Catalytic

radial

*M, tsubishi
radial structure*

Related to them conductive.

and I will
with you

Note: Gauge Length: 20mm; No. of Filaments: 30

*Very high purity
carbon fibers*

*335 is perfect fit,
graphitic
crystal regions
rather*

X-ray diffraction data of carbon fibers carbonized at 2400°C

Type of Mesophase	d(00,2) (nm)	L _c (nm)	FWHM (°)
Heat-Soaked	0.3420	13.1	0.6666
Mitsubishi AR	0.3367	15.2	0.5769
Supercritical Extraction	0.3360	15.8	0.5643

*↑ for
increasing
purity
graphitic
regions*



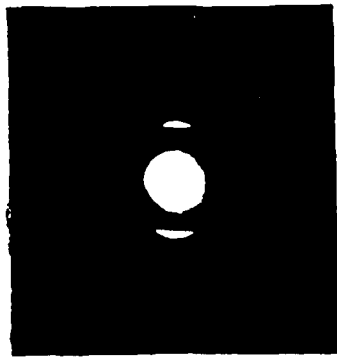
Longitudinal BF Image and SAD Pattern of Catalytic Mesophase Round Fiber

Pl. substrate
1000x

11 nm
slice

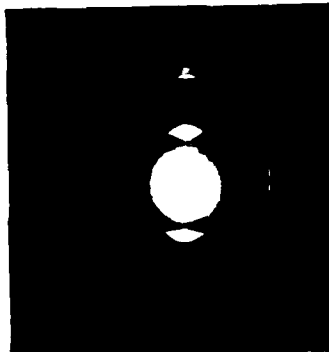
Selected area diffraction

SAD Patterns Taken From Longitudinal Sections of Round Fibers



Heat-Soaked

worst,



SCF-Extracted

*quadrants →
but
better than*



Catalytic

Mitsubishi

CONCLUSIONS

- **Petroleum Pitch can be Fractionated with SC Toluene in a Continuous-Flow Apparatus to Produce a 100% Mesophase Pitch**
- **The Denser, Pitch-Rich Phase in the LL Region Spontaneously Forms Mesophase Pitch Upon Flashing**
- **A Capacitance Technique has been Developed for Interface Detection**
- **Carbon Fibers Melt-Spun from a Mesophase Pitch Produced at 340 °C and 70 bar Exhibit Strengths and Moduli Equal to the Best Commercial Fibers**
- **Future Changes to SCF Extraction Apparatus are Required to Improve Mesophase Reproducibility**

CONCLUSIONS

- With These Fiber Properties and the Continuous Nature of the Process, SCF Extraction is an Attractive Low-Cost Alternative to Existing Pitch Treatment Processes

Can do
pitch amount
estimate
of
cost

72M/yr
PAN - 1000
\$5/lb.
for PAN.

1M16/yr

1M16/yr

Hopeful for
funding future

FUTURE WORK

- Improve Cell Design
- Automate Portions of SCF Extraction Apparatus
- Explore Effect of SCF Operating Conditions on Mesophase Formation and Resultant Fibers
- Produce Pitch Microfractions for Characterization
- Test SCF-Extracted Mesophase on a Pilot Scale

what about
MOR

but then
G.W.G.

have pilot
scale
spinning
facility
@ Clemson

II-L-40

Conoco willing to do
on pilot scale
& Clemson
spinning

ACKNOWLEDGMENTS

- E.I. du Pont de Nemours and Co.
- U.S. Army Research Office
- Defense Advanced Research Projects Agency
- Conoco Inc.

*not dollars
but price supplier -*

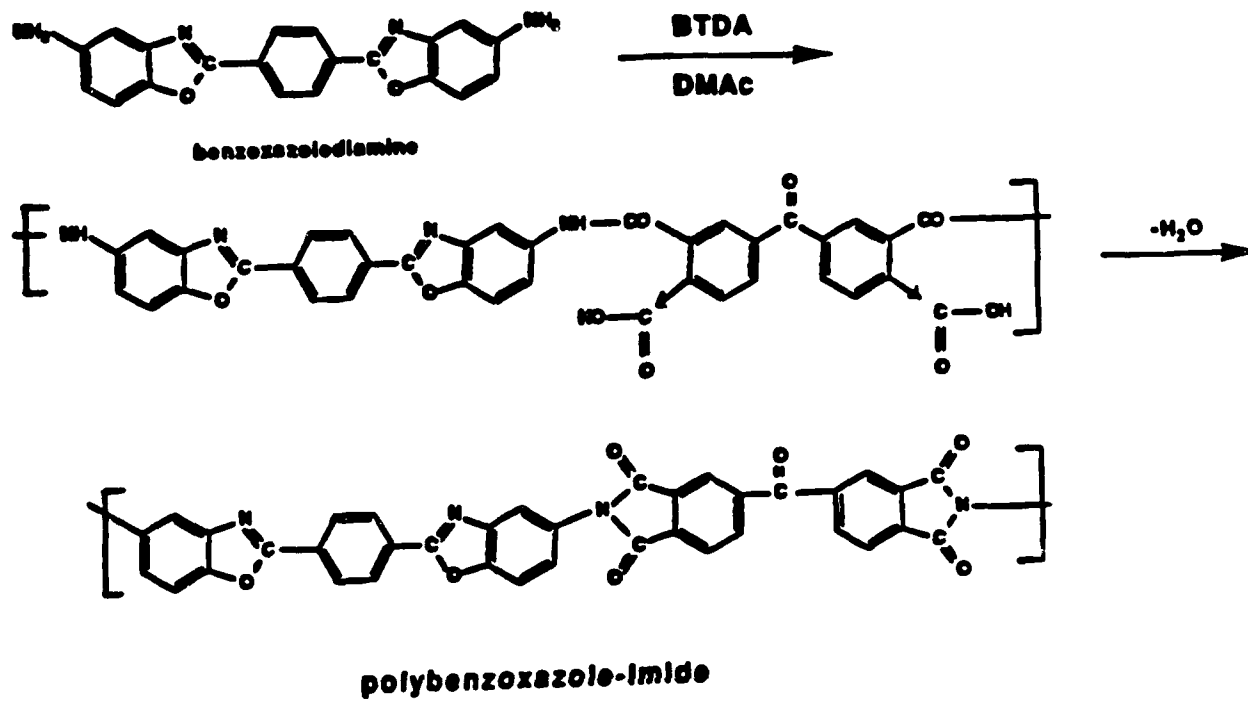
Conoco's goal is lower cost.

*GM - NY times
Am Lab Co*

RESEARCH TRIANGLE INSTITUTE

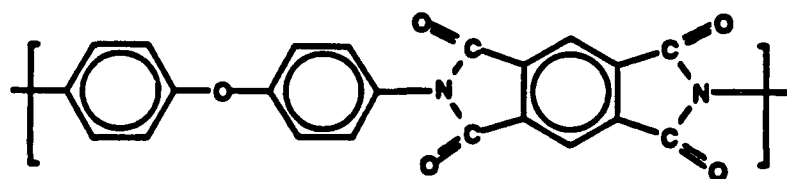
Dr. Jack Preston

II-M-1

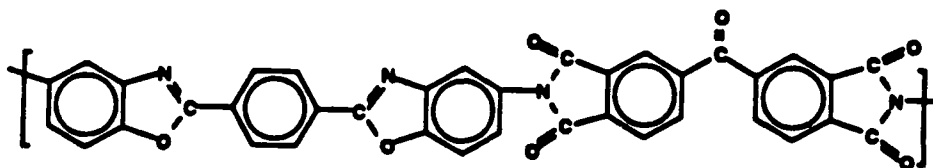


Thermooxidative Stability Comparison of Fibers from
Polymers III and IV.

Fibers Made From:	Number of Days at 300°C in Air		
	10	49	70
<u>Tenacity, % Retention</u>			
I	0.0	-	-
II	94	83	30
<u>Elongation, % Retention</u>			
I	0.0	-	-
II	78	62	26

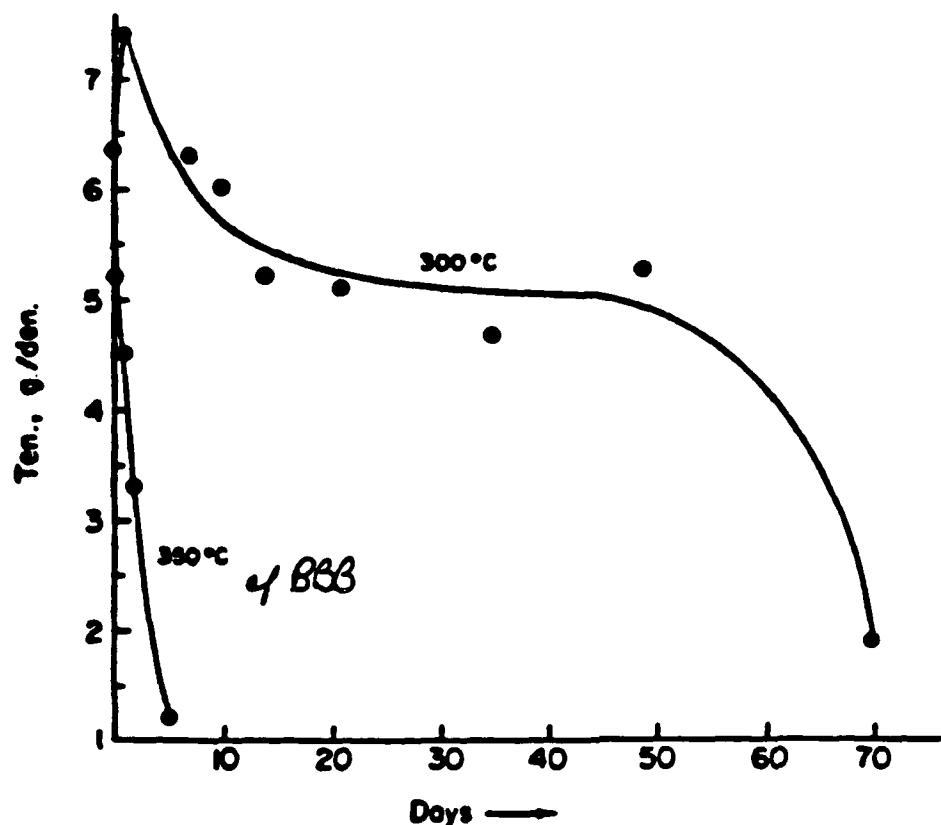


I

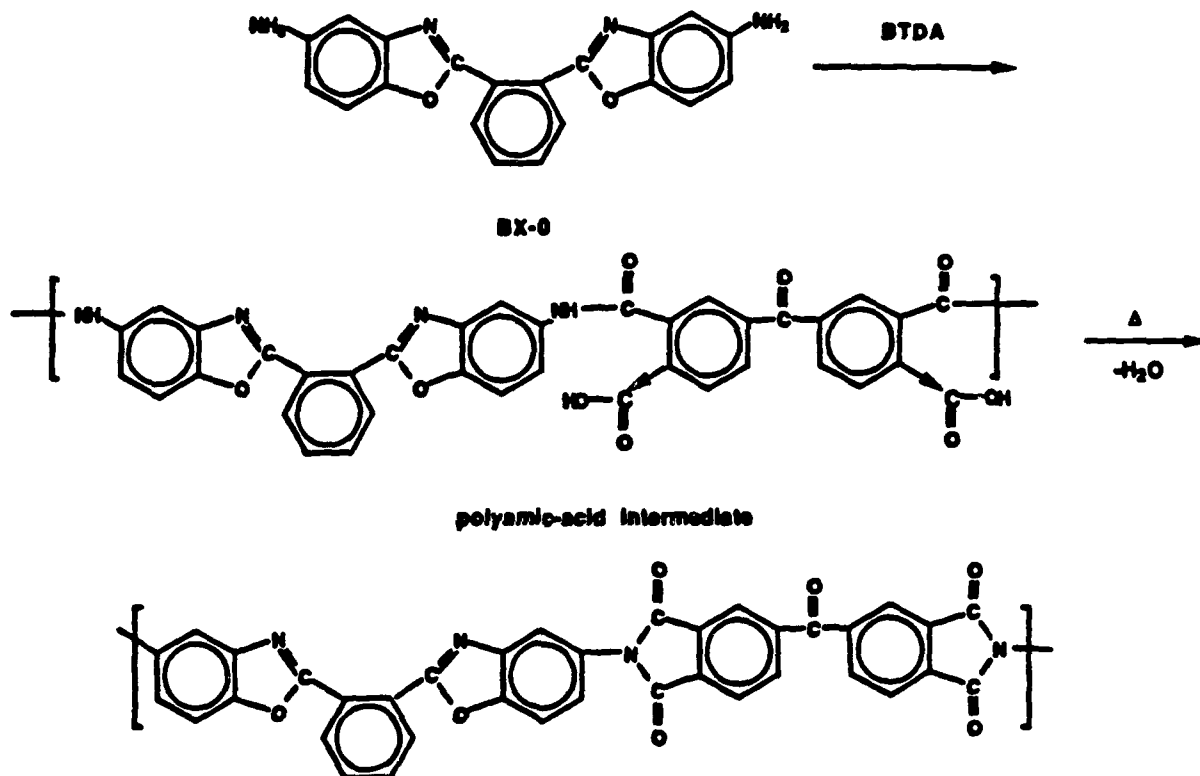


II

II-M-4



Retention of tenacity of benzoxazole-benzophenone-imide fibers after heat-aging in air.



This polymer shows a decomposition temperature of $\sim 550^\circ\text{C}$ by DSC and DTA!

Note: Very few heat resistant polymers have been reported having ortho-oriented rings because the synthesis usually would be prevented by chain terminating reactions producing imide groups, etc.

T_g

°C

DSC

290

TMA

(Fluorene)

283

TBA

180 to 300°C
increase temp

296 ← !

300 to -180

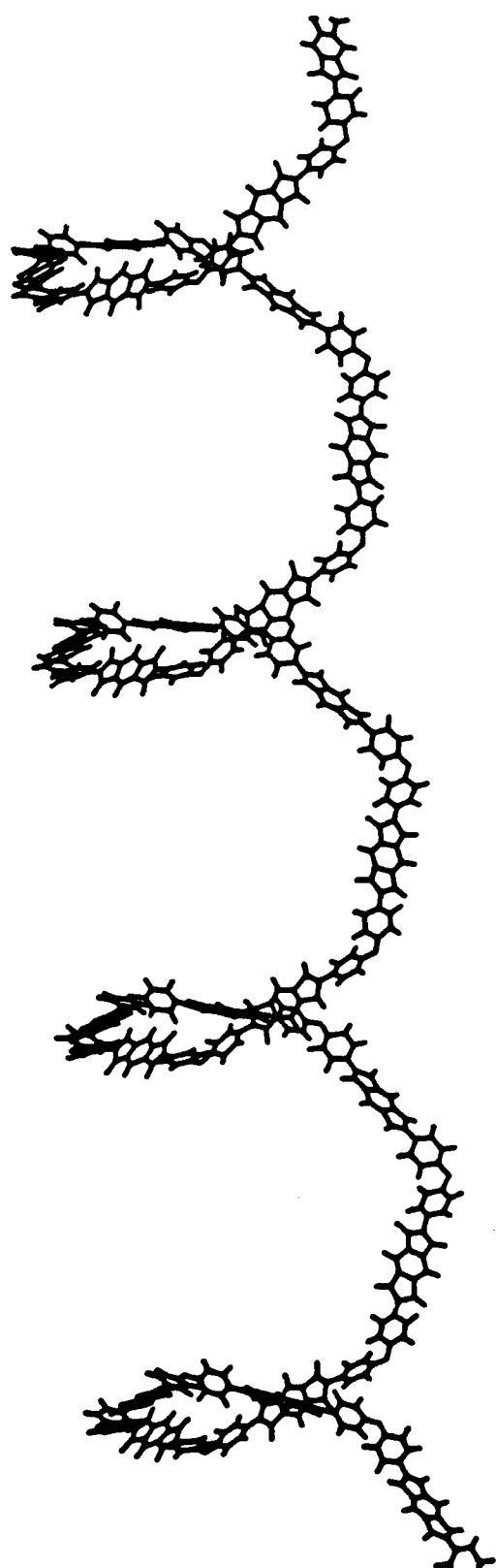
287

-180 to 350

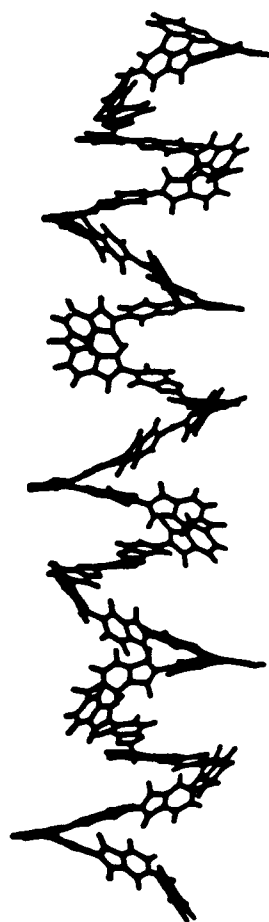
286

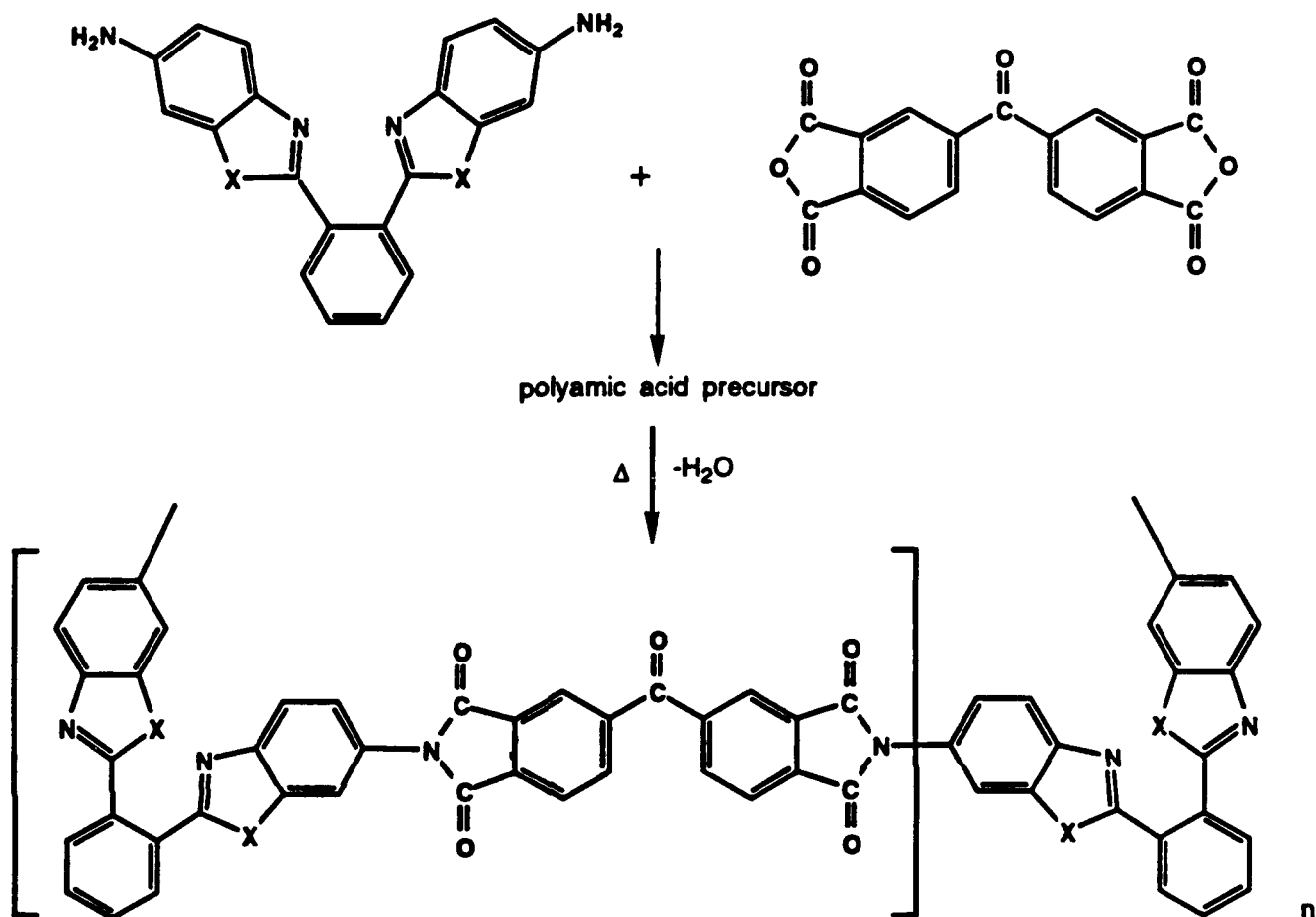
Notes: BTDA polyimides typically
show a T_g = 288°C.

$$T_g = \frac{2}{3} m.p. = \frac{2}{3}(570^\circ\text{C}) = 289^\circ\text{C}$$



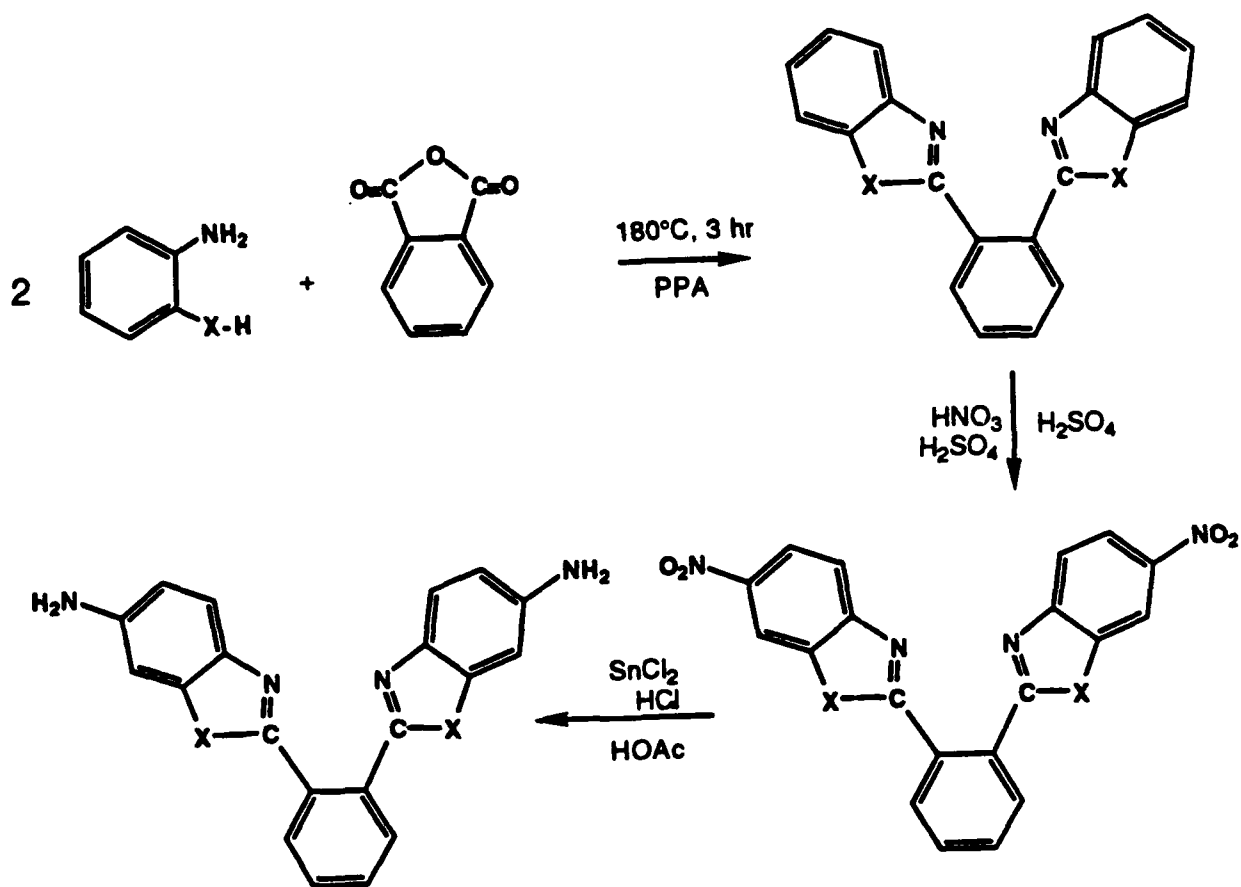
II-M-8



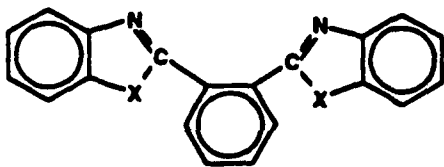




where $x = -\text{S}-, -\text{O}-$

maybe forming
 NLO material




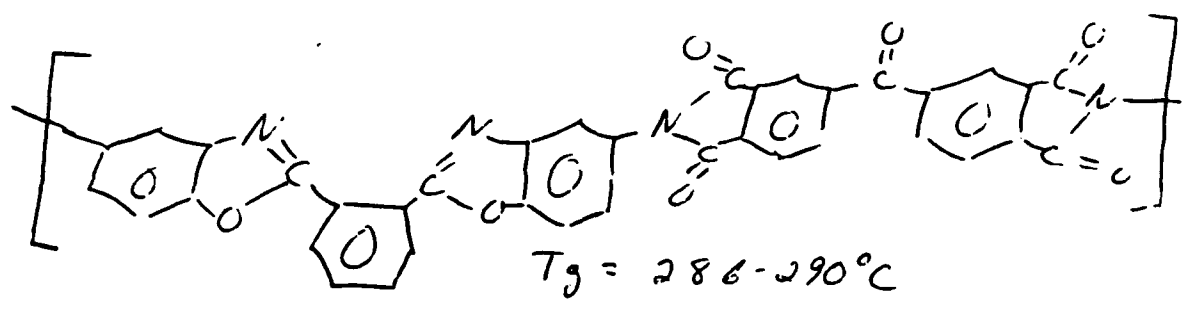
Melting Points of *bis*-Benzheterocyclic Model Compounds Containing Phenylene Rings.

Structure	m.p. (°C) ^{a,b}	
	X = S	X = O
	115.5 ¹⁴ (111.5-112.0) ¹⁵	179 ¹⁴ (177) ^{10,13}
	234.5 (229) ¹³	229 ¹⁴
	264.9 ¹⁴ (257-258) ¹⁵	(355-356) ¹³

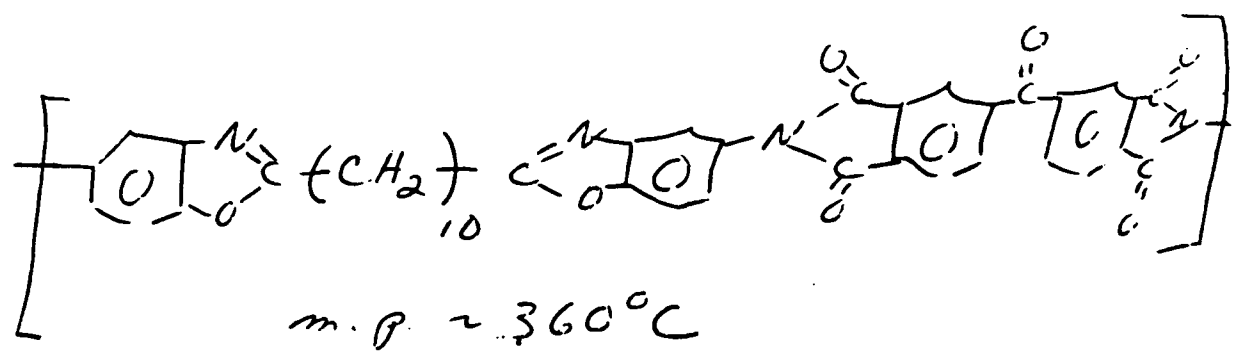
a Determined from the peak of the DSC curve for a sublimed sample.

b Values in parentheses are for recrystallized samples reported in the literature.

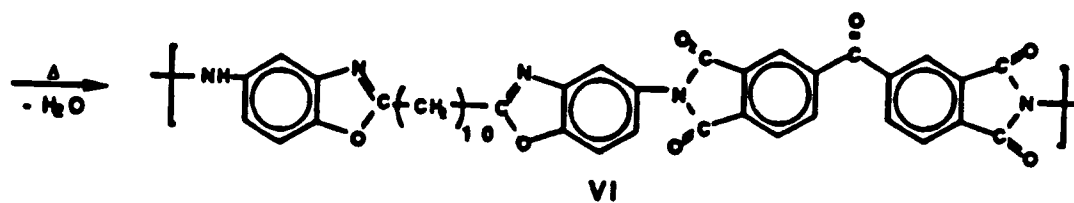
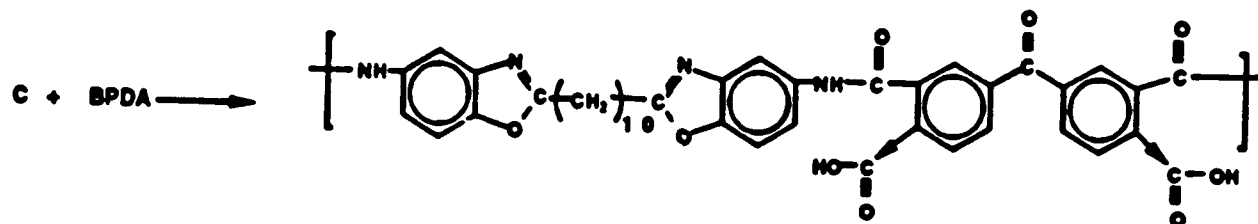
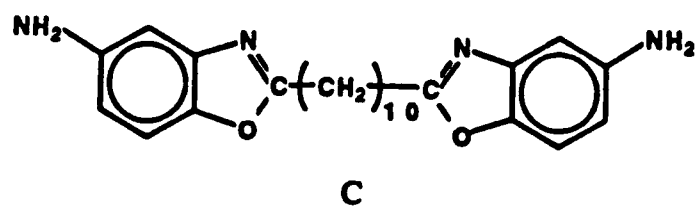
 thiophene (with Samulky)
241 225

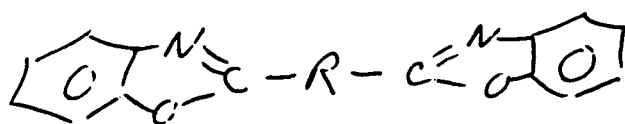
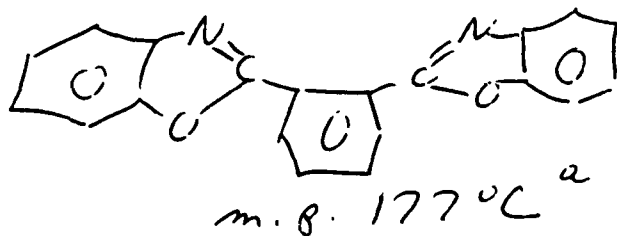


"pressable" at $\sim 310^{\circ}\text{C}$

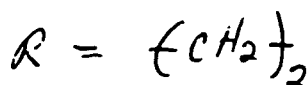


$T_g = \frac{2}{3} \text{ m.p.} = \frac{2}{3} (360) = 151^{\circ}\text{C}$

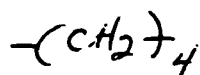




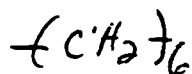
m. p., $^{\circ}\text{C}^a$



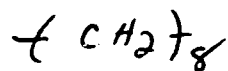
192-193



126-127

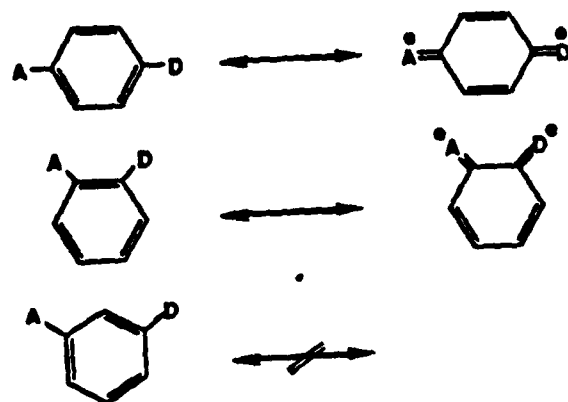


96-98



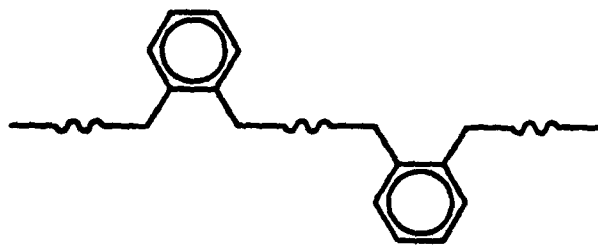
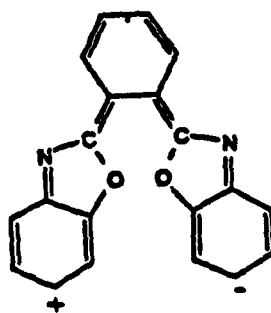
87-88

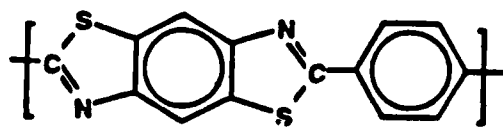
^a E. Nyilas and J. L. Pinter,
J. Am. Chem. Soc., 82, 609 (1960).



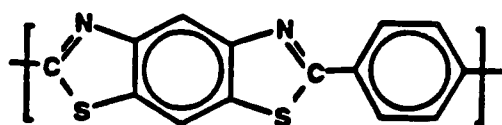
8/10/50

Ground-state and lowest energy polar resonance forms for p- and o-substitution. Resonance is forbidden in the case of m-substitution.

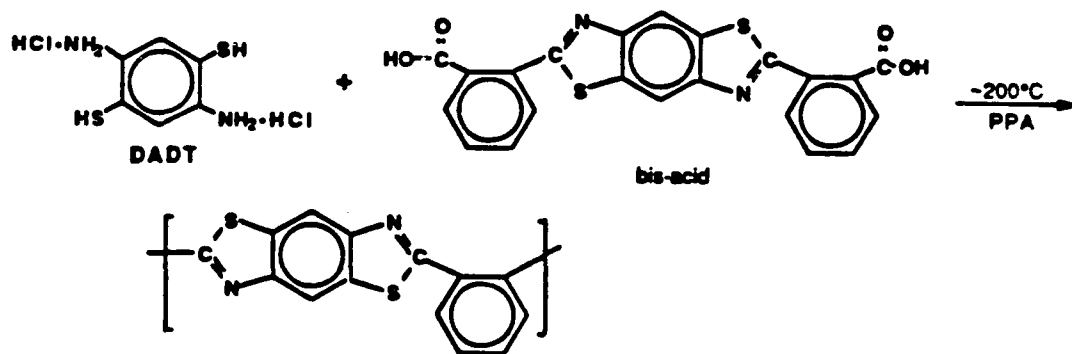




trans-PBT

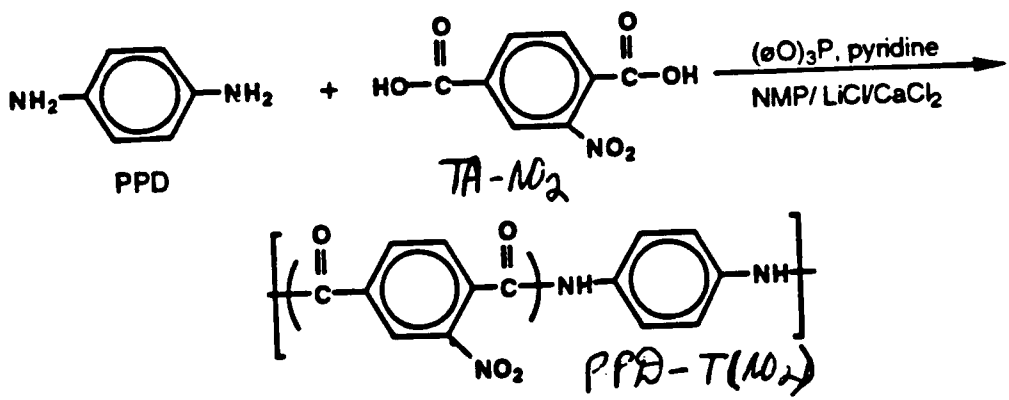


cis-PBT



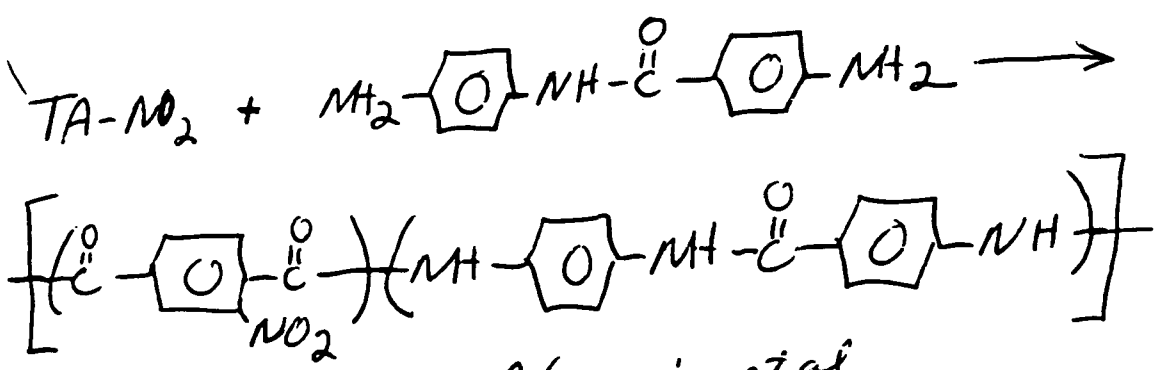
30% soluble
Removable

hard to synthesize
nitro



soluble in N-methylpyrrolidone (NMP) to 30% solids!

nitro is problem
acid

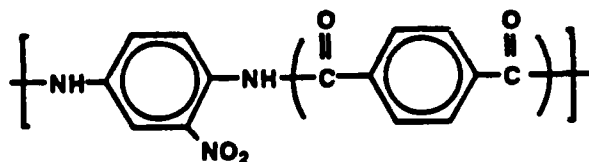


Akaroni et al

PPD-T/PPD-T(NO₂)
copolymer (1:1) not soluble
in NMP

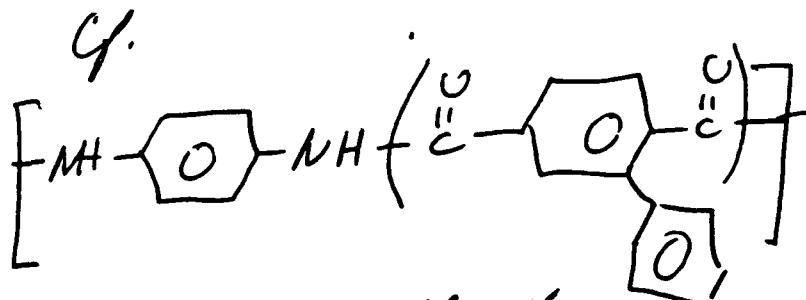
should be
OK

No longer
work

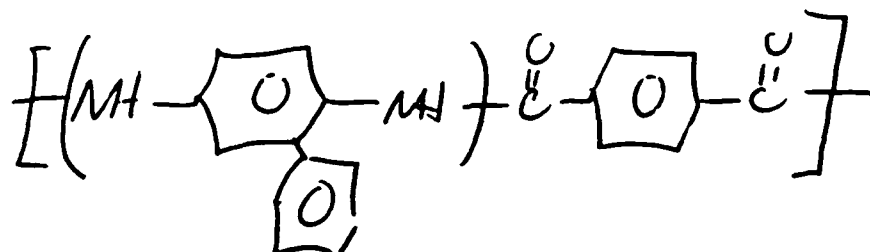


not soluble in NMP with added salts

change to 3rd pair



more soluble than:



on TA:



Work by :

Dr. J. W. Trexler, Jr.

Dr. Y. G. Tropsha

Dr. J. W. Carson, Jr.

Dr. P. K. Sripada